

Alec Groysman

Corrosion in Systems for Storage and Transportation of Petroleum Products and Biofuels

Identification, Monitoring and Solutions

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Preface

Fuels occupy one of the main places in the history of modern mankind. More than ever today it is impossible to imagine our life without fuels. You drive your car, fly by airplane, travel by ship, and warm your house using different fuels. In this book, we will talk only about liquid fuels producing from *petroleum products* (called also *distillates* or *refined products*), such as *liquefied petroleum gas* (LPG), *naphtha*, *gasoline*, *kerosene* (*jet fuel*), *gas oil* (*diesel fuel*), and *fuel oil* and corrosion in them. All these petroleum products are obtained from *crude oil*. We will also discuss corrosion in liquid *biofuels* which began occupy essential place in supply of energy and heat in many countries.

Metallic constructions for transportation and storage of crude oil, petroleum products and biofuels are made mainly from carbon steel. In spite of removing most corrosive species from fuels the paradox is that metallic constructions contacting with them are being damaged. Different polymeric and composite materials contact fuels. On the one hand, materials can deteriorate fuels. On the other hand, fuels can worsen important functional properties of materials. Therefore we will discuss metallic, polymeric and composite materials including organic coatings which also can contact fuels. Resistance of all these materials to fuels is very important in preserving both environment and fuels from deterioration. These problems can be sum up as following questions:

Why are crude oils, petroleum products, fuels and biofuels aggressive to metals, alloys and polymeric materials? Which corrosion control and monitoring methods are used in order to prevent corrosion failures in systems for transportation and storage petroleum products?

In this book, I summarized experience based on my long practical and research work, as well numerous literature data which are collected and analysed.

Thus I invite you to the marvelous world of liquid fuels, their aggressiveness, corrosion control and monitoring methods.

*To my great, wise, intelligent and smart
wife Olga for constant support, endurance,
understanding and assisting in creating,
discussing and writing this book, and also
to my lovely children Sasha, Anat, Tal and
beautiful grandchildren Jonatan and Ido*

*“I believe that getting to know more and more,
a man acquires infinite power.”
Émile François Zola (1840–1902), a French writer*

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List of Abbreviations

AE	Acoustic Emission.
ANSI	American National Standards Institute.
API	American Petroleum Institute.
API RP	American Petroleum Institute Recommended Practice.
AR-AFFF	Alcohol-Resistant Aqueous Film-Forming Foam.
AR-FFFP	Alcohol-Resistant Film-Forming Fluoroprotein Foam.
ASA-3	Anti-static additive of Shell Oil Company.
ASNT	American Society for Nondestructive Testing.
ASTM	American Society for Testing and Materials (ASTM International).
Avgas	Aviation gasoline.
B20	Fuel blend containing 20 vol% biodiesel and 80 vol% conventional diesel fuel.
B100	Neat biodiesel.
BTX	Benzene, Toluene, Xylene.
BTEX	Benzene, Toluene, Ethyl benzene, Xylene.
CFU/ml	Colony Forming Units per milliliter of liquid; an estimate of viable bacterial or fungal numbers.
CI	Compression Ignition, i.e. a diesel engine.
CIPS	Close Interval Potential Survey.
CU	Conductivity Unit.
DCVG	Direct Current Voltage Gradient.
DI	Direct Injection.
Di-EGME	Diethylene glycol monomethyl ether.
DIN	Deutsches Institut Fur Normung E.V. (German National Standard).
DS	Data Series.
EC	Eddy Current.
EDS	Energy Dispersive Spectroscopy.
EEMUA	The Engineering Equipment and Materials Users' Association.
EGME	Ethylene glycol monomethyl ether.
EI	Energy Institute (formerly IP—Institute of Petroleum), England.
E10	Fuel blend containing 10 vol% ethanol and 90 vol% gasoline.
E85	Fuel blend containing 85 vol% ethanol and 15 vol% gasoline.

EN	European Norm, European Standard.
EPS	Extracellular polymeric substances.
ETP	Type of Viton.
Euro 5	European emission standard.
FAME	Fatty Acid Methyl Ester.
FAEE	Fatty Acid Ethyl Ester.
FBE	Fusion Bonded Epoxy.
FGA	Fuel Grade Alcohol.
FRP (GFRP, GRP)	Fiberglass Reinforced Plastic.
FSII	Fuel System Icing Inhibitor.
FSM	Field Signature Method.
GFRP (see GRP, FRP)	Glass-fiber reinforced plastic.
GRP (see GFRP, FRP)	Glass-reinforced plastic.
GTBA	Gasoline grade <i>t</i> -butanol; named also Tertiary-Butyl Alcohol (TBA).
HC	Hydrocarbons.
HDPE	High Density Polyethylene.
HDS	Hydrodesulfurizer.
HE	Hydrogen Embrittlement.
HUM bugs	Hydrocarbon Utilizing Microorganisms.
ICP	Inductively Coupled Plazma.
IDI	Indirect Injection.
ILI	In-line inspection.
IMPCA	International Methanol Producers & Consumers Association.
IOB	Iron-oxidizing bacteria.
IP	(<i>see EI</i>).
IPA	Isopropanol.
IPC	Ion Plazma Couple.
IR	Infrared.
ISO	International Organization for Standardization.
IUPAC	International Union of Pure and Applied Chemistry.
kPa	Kilo Pascal.
KWA	Ken Wilcox Associates Inc.
LL	Low lead.
LPG	Liquefied petroleum gas.
M15	Fuel blend containing 15 vol% methanol and 85 vol% gasoline.
M85	Fuel blend containing 85 vol% methanol and 15 vol% gasoline.
M100	Fuel containing 100 vol% methanol.
MFL	Magnetic Flux Leakage.
MTBE	Methyl Tertiary-Butyl Ether.
NA	Naphthenic acids.

NACE

International	National Association of Corrosion Engineers International.
NBR	Nitrile Butadiene Rubber (Buna-N).
NDA	Nitrite Dicyclohexylamine.
NDT	Non-Destructive Technique.
NFPA	National Fire Protection Association.
NLPA	National Leak Prevention Association.
NR	Natural Rubber.
PA	Polyamide (Nylon 6), polymer.
PE	Polyethylene.
PEC	Pulsed Eddy Current.
PEI	Petroleum Equipment Institute.
PP	Polypropylene.
PVC	Polyvinyl Chloride.
ppb	Parts per billion; weight concentration; 1 mg of substance (solute) in 1,000,000,000 mg (1,000 kg) of solution.
ppm	Parts per million; weight concentration; 1 mg of substance (solute) in 1,000,000 mg (1 kg) of solution.
psi	Pounds per square inch.
pS/m	Pico Siemens per meter.
RCM	Resistance Corrosion Monitoring.
SEM	Scanning Electron Microscope.
S/m	Siemens per meter.
SFGA	Synthetic Fuel Grade Alcohol.
SP	Standard Practice.
SRB	Sulphate Reducing Bacteria.
SCC	Stress Corrosion Cracking.
SSPC	Steel Structures Painting Council.
STI	Steel Tank Institute (USA).
TAME	Tetra amyl methyl ether.
TAN	Total Acid Number.
TBA	Tertiary-Butyl Alcohol; named also Gasoline grade <i>t</i> -butanol (GTBA).
TBC	Total Bacteria Count.
TEL	Tetra-Ethyl Lead.
TM	Test Methods.
TPC	Total Plate Count.
UL	Underwriters Laboratory Inc.
UV	Ultra Violet.
ULSD	Ultra Low Sulphur Diesel Fuel (less than 10 ppm sulphur).
UNS	Unified Numbering System.
UT	Ultrasonic testing.
US	Ultrasound.
UST	Underground Storage Tank.
VCI	(VPI, VpCI) Vapor (Volatile) Corrosion Inhibitors.

VOC	Volatile Organic Compounds.
Vol%	Volume percent.
VpCl	see VCl.
VPI	see VCl.
Wt%	Weight percent.

About the Author



Dr. Alec Groysman graduated in 1973 from the Chemico-Technological University named after Mendeleev in Moscow. He received his Ph.D. in physical chemistry and corrosion in 1983 in Moscow. He has experience in corrosion and protection from corrosion from 1976 in the oil refining industry.

He deals with kinetics and thermodynamics of corrosion processes, on-line corrosion monitoring, choice and use of corrosion inhibitors, coating systems, selection of appropriate alloys for corrosive conditions, and failure analysis.

He has special interests in corrosion education and in the searching of relationships between corrosion, art, history and philosophy.

His first book “Corrosion for Everybody” published by Springer in 2010 received the innovation award winner of Materials Performance Readers’ choice in 2012 year in the USA.

He is a lecturer of the courses “Corrosion and Corrosion Control”, “Physical Chemistry”, and “Materials and Standards in Oil and Gas Engineering” in the Technion (Haifa) and in the ORT BRAUDE college of engineering in Karmiel in Israel.

Chapter 1

Physico-Chemical Properties and Corrosiveness of Crude Oils and Petroleum Products

Knowledge is always good. It may one day come in handy.

Folk wisdom.

Abstract Crude oil characteristics, chemical compounds containing in crudes and their corrosiveness are described. Physico-chemical characteristics of *petroleum products*, such as *liquefied petroleum gas* (LPG), *naphtha*, *gasoline*, *kerosene* (*jet fuel*), *gas oil* (*diesel fuel*), and *fuel oil* obtained from *crude oil* also are analysed. Differentiation between the terms *fuel* and *petroleum product* is given. It is shown which components in crudes and petroleum products are corrosive. Corrosiveness of petroleum products is explained by the presence of water and dissolved oxygen. Water can be present as dissolved, emulsion water-in-fuel and free water in petroleum products. Solubility of water depends on temperature, relative humidity of air with which fuels contact, and fuel composition. Water solubility in fuels is greatly influenced by the presence and concentration of aromatic and olefin compounds. The free water is most dangerous in the occurring corrosion. Experimental data of solubility of oxygen in liquid petroleum products, fuels, alcohols, biofuels, their components, and, for comparison, in water are given. The methods of removing dissolved oxygen from fuels are described. Formation of aggressive compounds to metals and polymers as a result of oxidation of hydrocarbons containing in fuels also is described. Definition of corrosiveness of petroleum products is given.

In order to understand why corrosion can occur in petroleum product systems, we begin by defining corrosion and petroleum products. *Corrosion is an interaction between a material, usually a metal, and its environment that results in deterioration of the material and the environment.* The term *environment* refers to crude oils, petroleum products, fuels, fuel additives, biofuels, and other components (oxygenates and organic solvents). Below we describe their physico-chemical properties and interaction with metals and polymers.

First, let us differentiate between the terms *fuel* and *petroleum product*. *Fuel* is any material that stores energy that can later be extracted to perform mechanical work or provide heat. Many types of gaseous (natural gas, and hydrogen gas), liquid (petroleum products, liquid hydrogen, liquid alcohols and esters, substances produced from coal and shale by pyrolysis) and solid fuels (wood, coal, peat, shale, lignite, radioactive metals) exist.

Crude oil, a mixture of different liquid hydrocarbons that exist in the Earth's crust, undergoes distillation, whereby the liquid homogenous mixture is separated into fractions based on differences in boiling points of its components. As a result of the distillation process, the following petroleum products are produced: *liquefied petroleum gas* (LPG), *naphtha*, *gasoline*, *kerosene*, *gas oil (diesel fuel)*, *fuel oil*, and *bitumen (asphalt)*. These petroleum products obtained immediately after distillation are not yet the fuels that are used in cars, ships, and aircraft. Some of these, fuel oil and bitumen, can be used in furnaces and for road pavement without undergoing any other processing. Bitumen, in fact, is not fuel at all. Only after treatment, purification and other processes carried out in oil refineries, such as cracking, catalytic reforming, isomerization, hydrogenation, hydrocracking, sweetening, and clay treatment, do petroleum distillates become fuels.

Each petroleum product undergoes a different process. LPG is washed by an alkali solution. Naphtha is not used as a fuel, but is very similar to gasoline in content. It is an intermediate petroleum product used as the feedstock for obtaining high octane gasoline and olefins. Kerosene is treated and transformed into jet fuel; gasoline is also treated and transformed partly into gasoline for motor vehicles and aviation gasoline (avgas) for aircraft; gas oil is processed into diesel fuel. For convenience, when using the term *fuels* here we also mean *petroleum products*.

Corrosion of metals (as well resistance of polymeric materials) in liquid fuels and biofuels will be discussed in this book. We now describe the chemical compounds comprising crude oils, some of which cause corrosion in fuels.

1.1 Crude Oil Characteristics

1.1.1 Chemical Compounds in Crude Oils

Crude oil (often used shortly as *crude*) was formed from organic matter (planktonic plants and animals) in aquatic deposits over a period of million of years. The chemical composition of crude oils from different producing regions, and even from within a particular formation, can vary tremendously. Crude oils are complex mixtures of different chemical compounds mostly hydrocarbons over wide boiling range. The detailed analysis of chemical composition of crude oils and petroleum products is given in Appendix A. Following chemical compounds are contained in crudes:

- Alkanes (called also aliphatic hydrocarbons or paraffins) are saturated hydrocarbons, non-cyclical, *n*-alkanes (normal alkanes) and iso-alkanes (branched alkanes).
- Cycloalkanes (called also cycloparaffins or naphthenes).
- Crude oils generally contain no alkenes. Alkenes (called also olefins) are unsaturated hydrocarbons (e.g., $R-C=C-R$). *R* is radical C_nH_m (*n* and *m* are amounts of carbon C and hydrogen H atoms respectively). Alkenes are formed in oil refining units and are contained in gasoline (to 25%) and kerosene (to 5%).
- Aromatic hydrocarbons (called shortly aromatics) contain one or more aromatic (benzene) rings. Like alkenes, they are unsaturated hydrocarbons. Usually aromatics are less abundant than the saturated hydrocarbons.

- e. Waxes (un-branched n-alkanes with up to C_{30} carbon atoms).
- f. Heteroatomic organic compounds containing sulphur, nitrogen, and oxygen atoms.
- g. Dissolved hydrocarbon gases (methane CH_4 , ethane C_2H_6 , propane C_3H_8 , and butane C_4H_{10}) and hydrogen sulphide (H_2S).
- h. Metals: generally vanadium (V), nickel (Ni); sometimes also iron (Fe), aluminium (Al), sodium (Na), potassium (K), calcium (Ca), and copper (Cu).

Not all compounds containing in crudes are corrosive and aggressive to metals, alloys, and polymers (Appendix B). We will discuss in the next section which compounds in crudes are responsible for their corrosiveness and aggressiveness.

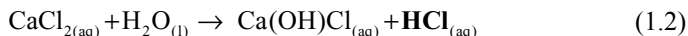
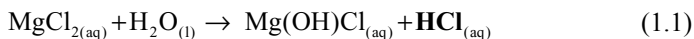
1.1.2 Corrosive Characteristics of Crude Oils

Because crude oil is a mixture of widely varying constituents and proportions its physico-chemical properties also vary widely. Most organic compounds containing in crude oils are not corrosive to metals and alloys (see Appendix B). Crude oils are not corrosive at ambient temperatures. Even certain crudes can inhibit corrosion of metals because of organic constituents adsorbing on metal surface, modifying the corrosion products and forming a protective layer. Crude oils can become corrosive when they are heated in refineries. Crude oils can contain water, inorganic salts dissolved in water, hydrogen sulphide, organic compounds containing nitrogen, oxygen and sulphur, small amounts of metals, solid particles, and microorganisms. Corrosion characteristics of crudes are defined by total sulphur (S) content, total acid number (TAN), salt and water content, and microorganisms. These species influence corrosion by different manner and at different stages of preparation, transportation, storage, and distillation of crudes. Water has limited solubility in hydrocarbons and the presence of free (undissolved) water is necessary for corrosion. For instance, limiting amount of salt and water is $< 1\%$ (often $< 0.5\%$) in crude oils in transmission pipelines. Otherwise, the solid particles tend to be encapsulated by a layer of water on the pipe surface. Water drop-out and accumulation can occur at low velocities and under stagnant conditions.

Total sulphur content is used to characterize potential corrosion by various organic sulphur-containing compounds and hydrogen sulphide. The latter is the main corrosive agent among sulphur-containing compounds that are present in crude oils and influences corrosion at all stages of output, transportation, storage and treatment of crudes. Total acid number (called also neutralization number) is a measure of the numbers of milligrams of potassium hydroxide (KOH) needed to neutralize 1 g of crude or its distillate fraction. TAN values are used to characterize corrosiveness of crudes and their distillate fractions because of the presence of organic acids (including also naphthenic acids) which mostly corrosive during distillation and further transportation of some petroleum distillates (gas oil and fuel oil) at temperatures $190\text{--}360^\circ\text{C}$ in refineries.

Inorganic Compounds in Crudes Inorganic chloride salts ($NaCl$, $MgCl_2$, $CaCl_2$), hydrogen sulphide (H_2S) and elemental sulphur (S_8) are main corrosive species

in crudes. Chloride salts when they are present in aqueous solution in two-phase crude-water system are very corrosive to carbon steel. Amounts of these salts differ significantly from one type of crude to another. Usually the ratio of these salts is: 75% NaCl + 15% MgCl₂ + 10% CaCl₂. Sodium chloride (NaCl) is corrosive in concentrations which are in crude oils. Two other salts, MgCl₂ and CaCl₂, are hydrolyzed with formation of hydrochloric acid (HCl). High temperature in distillation columns stimulates hydrolyzation of MgCl₂ and CaCl₂.



They can hydrolyze in mixtures crude-water during transportation, storage, and then in distillation columns at oil refineries. The media in all cases will be acidic and very corrosive as pH decreases to 1–2.

Sulphur and Sulphur-Containing Compounds Crude oils differ significantly in content of sulphur-containing compounds. For instance, the crude in Etzel (Germany) contains the highest concentration of sulphur –9.6%; its kerosene fraction (190–240 °C) contains 6.6% S, light gas oil (220–360 °C) –9.15% S, and asphalt –10.8% S. In contrast, some crudes in Australia, Saratov and Sakhalin (Russia), Ukraine and Kazakhstan contain very low concentration of sulphur, 0.1–0.2% S. Low concentration of sulphur (0.9%) is present in crude in Tyumen (West Siberia, Russia); it is unique as the most sulphur compounds are concentrated in gasoline, and mercaptans contain a half of these sulphur compounds.

Crudes containing large amounts of sulphur are called ‘sour crudes’. The most common form of sulphur in crudes is hydrogen sulphide (H₂S). The gas H₂S (at ambient temperatures) is colorless, highly toxic, and its releases can cause death within seconds. You can detect this poisonous gas according to specific smell of rotten eggs.

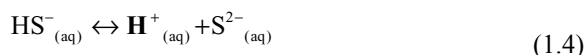
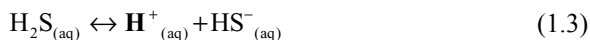
Composition and content of sulphur-containing compounds in petroleum products depends on type of crudes and the procedure of their treating.

Molecular sulphur (S₈), hydrogen sulphide and organic sulphur-containing compounds (mercaptans, aliphatic sulphides, and polysulphides) can be present in crude oils (see Appendix A). They are divided on highly corrosive (sulphur as element, hydrogen sulphide, and mercaptans), corrosive (sulphides and disulphides) and non-corrosive (alkyl thiophenes and alkyl benzothiophenes) (see Appendix B). Even their corrosiveness is realized not under all conditions; really they are corrosive under appropriate concentrations and temperatures. Some of them (polysulphides) can be corrosion inhibitors.

Sulphides and mercaptans are main corrosive substances in petroleum products. The relative corrosivity of sulphur-containing compounds usually increases with temperature rising. With the exception of thiophenes, sulphur-containing compounds react with metal surface at elevated temperatures, forming metal sulphides, certain organic molecules, and hydrogen sulphide. Uniform corrosion, pitting

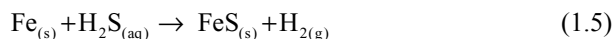
corrosion and erosion-corrosion can occur under attack by sulphur-containing compounds. Corrosion rate depends on the formation of sulphide scale. Sometimes the iron sulphide scale formed on carbon steel surface can serve as passive layer protecting metallic constructions from further corrosion in liquid hydrocarbon phase. Usually iron, carbon steel, nickel, copper and their alloys are not resistant to sulphur compounds, especially at high temperatures. Chromium, iron-chromium steels (containing > 1.25% Cr), aluminum, and stainless steels are resistant to this attack. We will describe separately corrosivity of sulphur, hydrogen sulphide, and organic sulphur-containing compounds.

Elemental Sulphur and Hydrogen Sulphide H_2S is present in ‘sour crudes’ and partly it removes with wash water in desalters. During distillation of crudes, H_2S dissolves in all fractions (petroleum products). H_2S also can be formed during destruction of organic sulphur-containing compounds at high temperatures which can be present in relatively high concentrations (hundreds and thousands ppm) in gasoline and naphtha. H_2S dissolves well in water. One liter of water can dissolve 3 l of H_2S with formation of weak acid:



Hydrogen sulphide acid is a weak acid, and $pH=4$ of 0.17% wt. H_2S aqueous solution. In spite of colorless anions S^{2-} and HS^- their salts have different colors. Most sulphides are black. Some of them (FeS , ZnS , and MnS) are undissolved in water but are dissolved well in weak hydrochloric acid (HCl). Another group (CuS , PbS) is undissolved both in water and weak HCl . This fact is important when different metals corrode in the presence of H_2S and sulphides are formed on the metal surface.

Solubility of H_2S in organic solvents is significantly more than in water (Appendix C). For instance, solubility of H_2S in hydrocarbons is 4–6 times and in alcohols 3.5 times greater than in water. Increase of temperature results in decrease of solubility of H_2S in solvents. H_2S reacts with iron and causes its corrosion:



Hydrogen sulphide like oxygen has two “corrosion faces”. As a result of iron corrosion by H_2S passive layer of iron sulphide (FeS) is formed on the iron surface. If this layer is even and thin (thickness of 5–10 μm) it protects iron surface from further corrosion. However, if the layer of iron sulphide is uneven and thick (thickness above 80 μm), localized corrosion can occur under the passive layer.

Hydrogen sulphide is the main cause of corrosion of inner surfaces of bottoms and roofs in tanks containing ‘sour crudes’, and roofs in tanks containing gas oil and fuel oil (see Sect. 5.8).

Hydrogen sulphide is removed with gaseous hydrocarbon products during distillation of crude oil and through their alkali treating. Certain sulphur-containing

organic compounds can be reduced to elemental sulphur (S_8) under high temperatures, pressures and in the presence of catalyst. Then this sulphur can dissolve in petroleum products. Both hydrogen sulphide and elemental sulphur are highly corrosive to iron, copper, nickel and their alloys. Therefore both H_2S and elemental sulphur must be absent in fuels.

Organic Sulphur-Containing Compounds The corrosivity of organic sulphur-containing compounds depends on their chemical structure. During distillation of crudes sulphur-containing compounds are concentrated unevenly in distillate fractions (petroleum products). Content of corrosive organic sulphur-containing compounds increases with increasing boiling point of distillate fractions. Thus, they are mostly concentrated in petroleum products with higher boiling point. The more boiling points of petroleum products the more is the total sulphur content. Mercaptans, especially aromatic mercaptans, are most corrosive to carbon steel. For instance, gas oil containing mercaptans is 3–4 times more corrosive than the gas oil containing sulphides or thiophenes in amounts 80 times more than the concentrations of mercaptans. Such corrosivity is explained probably not by organic sulphur-containing compounds themselves, but by sulphuric and sulphonic acids formed as a result of oxidation of mercaptans.

Sulphur-containing compounds that are present in petroleum products are especially corrosive at temperatures between 260 and 540 °C. As a result of purification processes at oil refineries sulphur-containing organic compounds are destroyed to hydrogen sulphide. Small concentrations of H_2S remain in gas oil and fuel oil. These remainders of H_2S cause severe corrosion of inner surfaces of roofs in storage tanks containing gas oil and fuel oil.

Organic Oxygen-Containing Compounds Alcohols (ROH), aldehydes ($RCHO$), ketones ($RCOR_1$), organic acids (having the carboxylic group – $COOH$), esters ($RCOOR_1$), ethers (ROR_1), phenol (C_6H_5OH) and its derivatives (cresols and others) are related to oxygen-containing organic compounds. Among these compounds only organic acids and sometimes small amounts of phenols can be present in crude oils. Others can be formed as a result of oxidation of various hydrocarbons and can be present only in petroleum products.

According to IUPAC (International Union of Pure and Applied Chemistry), the term ‘*organic acids*’ applies to a broad range of organic compounds which contain the organic acid group – $COOH$:

- aliphatic (fatty) acids $RCOOH$, where R is a straight $CH_3(CH_2)_n$ or branched chain;
- aromatic acids: $ArCOOH$, where Ar is a benzene ring or substituted benzene rings;
- naphthenic acids (NA): $XRCOOH$, where X is a cycloparaffinic ring; the chemical formula of NA is $X(CH_2)_nCOOH$ ($n \geq 0$) (see Appendix B).

All these three groups of organic acids can be present in crude oils, are stable and pass into petroleum distillates. Organic acids are distributed unevenly in petroleum distillate fractions, and, as a result, their corrosiveness is usually also different.

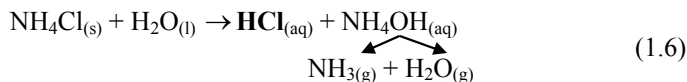
The TAN shows general content of all acids (organic and inorganic) which are present in crudes and petroleum distillates. Thus even wick acids, such as H_2S and mercaptans (R-SH) are included in the TAN. This value indicates to the crude oil refinery the potential of corrosion problems. Sometimes there is no correlation between TAN of crude oils/distillates and their corrosiveness. Some rules of thumb exist. It was suggested to use a threshold of 0.5 mg KOH/g of crude oils and of 1.5 mg KOH/g of petroleum distillates. Certainly, these values should not be used as absolutes. There are about 100 problematic high acidic crude oils ($\text{TAN} > 0.5$ mg KOH/g crude oil), and their geography is very diverse: Romania, Russia, Azerbaijan, Texas, California, the Gulf Coast, Canada, Venezuela, Columbia, Brazil, North Sea (Norway), West Africa (Congo, Nigeria), India, Indonesia, China, and Far East.

It is wrong to think that all organic carboxylic acids are corrosive. Some of them and their derivatives work as corrosion inhibitors. However, general rule is that the low molecular weight organic acids (formic and acetic) are more corrosive than high molecular weight organic acids. Naphthenic acids (NA) containing in some crudes represent large corrosive danger for oil refineries. $\text{TAN} = 220\text{--}320$ mg KOH/g for most pure NA. They are corrosive at $190\text{--}360^\circ\text{C}$ to carbon steels and low alloy steels (containing 1.25–5% Cr). Usually NA are concentrated in highly boiling distilled fractions (gas oil) and can corrode inner surfaces of distillation columns and pipelines ($\sim 350\text{--}360^\circ\text{C}$). Some crudes, for instance from Azerbaijan, contain light naphthenic acids concentrating in kerosene fraction ($190\text{--}210^\circ\text{C}$). NA that pass from crudes into petroleum products are not corrosive at ambient temperatures ($\sim 20^\circ\text{C}$) of their storage and transportation.

In petroleum products, in addition to organic acids with origins in crudes, different organic acids can appear as a result of decomposition of peroxides and hydroperoxides which can be formed by oxidation (by dissolved oxygen O_2) of hydrocarbons containing in petroleum products during their storage, distribution, and use. The amount of ‘new’ oxygen-containing compounds appearing in petroleum products during oxidation may be greater than that of original oxygen-containing compounds passing from crudes. Their content and composition depend on the presence of unstable organic compounds, duration and conditions of oxidation. Like sulphur-containing organic compounds, oxygen-containing compounds (mainly alcohols, ethers and substances with carbonyl group $\text{C}=\text{O}$) are concentrated in middle petroleum distillates ($150\text{--}350^\circ\text{C}$); their concentration in gasoline is very low. Phenols ($\text{C}_6\text{H}_5\text{OH}$ and its derivatives) in very small amounts exist only in some crudes. As a result of purification processes at oil refineries oxygen-containing organic compounds can be destroyed to H_2O and CO_2 which are corrosive to most metals.

Organic Nitrogen-Containing Compounds Following organic nitrogen-containing compounds can be present in crudes: pyridines, quinolines, alkylquinolines, benzoquinolines, acridines, pyrroles, indoles, carbazoles, benzo carbazoles, pyrrols, and amides. Not all these compounds are corrosive to metals. Even some of them are corrosion inhibitors, for instance, pyridine, some amides and their derivatives (see Appendix B). Organic nitrogen-containing compounds break down at high temperature and form ammonia (NH_3). Ammonia has “two corrosive faces”. On the

one hand, it works as corrosion inhibitor of carbon steel. On the other hand, ammonia reacting with hydrogen chloride in the overhead of distillation column can form deposits ammonium chloride (NH_4Cl) on metallic surface. This compound is hydrolyzed in the presence of water forming HCl (1.6) and causing corrosion under deposits both on carbon and stainless steel surface.



In addition, ammonia is corrosive to zinc, copper and their alloys.

1.2 Physico-Chemical Characteristics of Petroleum Products

Petroleum products are produced from many types of crude oils over the world and usually fuels as ending products are blended together to achieve desired physico-chemical properties. Petroleum products contain the entire hydrocarbon classes previously mentioned (see 1.1.1) but with narrower boiling ranges than corresponding crude oils. Thus petroleum products contain hundreds of non-polar hydrocarbons which differ by chemical structure and molecular mass (see Appendixes A and B). Olefins (alkenes and cycloalkenes) are absent in crude oils but appear in certain amounts in petroleum products as a result of cracking processes in oil refinery units (up to about 25 % vol. in gasoline). Alkylation processes at oil refineries yield many branched organic compounds such as iso-octane. We will describe each of petroleum products.

Liquefied petroleum gas (LPG) includes commercial butane (mixture consisting predominantly of butane and butene), commercial propane (mixture consisting predominantly of propane and propene), and mixtures thereof. LPG at normal atmospheric temperatures and pressure is a gas, but is readily liquefied under moderate pressure at ambient temperatures. It can be stored and handled as a liquid under pressure at ambient temperatures or under refrigerated conditions at atmospheric pressure. LPG is not corrosive to metals and alloys, but if water and chlorides are contained in LPG the latter may be corrosive to carbon steel (see Sect. 9); if water and washing soda (Na_2CO_3) products are contained in LPG the latter may be corrosive to aluminum alloys. Usually aqueous solutions of washing soda are corrosion inhibitors of carbon steel, but if chlorides (~ 0.1 % wt.) are present in this solution, corrosion rate of carbon steel reaches 1 mm/year at 25 °C.

Naphtha is the lightest and most volatile distillate fraction of the liquid hydrocarbons in crude oil. Three types of naphtha are differed. *Full range naphtha* is the fraction of hydrocarbons in crude oil boiling between 20 and 200 °C. It consists of a mixture of hydrocarbon molecules generally having between 5 and 12 carbon

atoms. *Light naphtha* is the fraction boiling between 20 and 90 °C and consists of molecules with 5 and 6 carbon atoms. *Heavy naphtha* boils between 90 and 200 °C and consists of molecules between 7 and 12 carbon atoms. Naphtha contains paraffins (65–85%), naphthenes (~30%) and aromatics (~5%) (see Appendix A). Corrosivity of naphtha is similar to that of gasoline. Usually inner surfaces of shells and floating roofs corrode in tanks containing naphtha.

Gasoline (named also *petrol*, *gas*, *motor gasoline*) is a liquid mixture of many different hydrocarbons boiling between 20 and 210 °C (see Appendix A). The carbon numbers range from 4 to 12, with the most prevalent carbon number being 8. Gasoline contains paraffins (~30%), aromatics (~35%), olefins (~25%; 18% according to EN 228 [1]), and naphthenes (~5%). The aromatic hydrocarbons benzene, toluene and xylenes are often referred to as BTX. They also contain ethylbenzene as well as three isomers of xylene (dimethylbenzene: meta-, ortho- and para-xylene). Sometimes this group of aromatics (benzene, toluene, ethylbenzene and xylenes) is referred as BTEX. 'Pure' dry gasoline and naphtha are not corrosive. If hydrogen sulphide, dissolved water, oxygen, and light organic acids are present in gasoline and naphtha these petroleum products become corrosive (see Sects. 1.2.1, 5.3 and 5.8).

Kerosene (*jet fuel*, *aviation turbine fuel*) is a liquid mixture of hydrocarbons boiling at 150–290 °C. The chemical composition depends on its source, and usually it consists of about tens different hydrocarbons, each containing 9–16 carbon atoms per molecule (see Appendix A). Kerosene contains paraffins (~45%), naphthenes (~35%) and aromatics (~20%). Kerosene can contain olefins (which are not present in original crude oils), organic sulphur- and oxygen-containing substances. Kerosene is less volatile than gasoline; its flash point (the temperature at which it will generate a flammable vapor near its surface) is between 37 and 65 °C, whereas that of gasoline is as low as –40 °C. Auto-ignition temperature of kerosene is 220 °C (the auto-ignition temperature of a substance is the lowest temperature at which it will spontaneously ignite in a normal atmosphere without an external source of ignition, such as a flame or spark). These properties make kerosene a relatively safe fuel to store and handle. We should mention, that liquid does not burn; only vapors can burn. And vapors do not always burn—the mixture of vapors and oxygen must be within the flammable range (definite ratio of volumes of hydrocarbon vapors and air). Aviation fuel is differentiated into avgas (aviation gasoline) and jet fuel. Avgas is the fuel suitable for piston engine aircraft where the emphasis is on anti-knock characteristics (see Sect. 2). *Jet fuel* is kerosene which is suitable for turbine engines.

Corrosive compounds such as dissolved water, molecular oxygen, organic acids, mercaptans and by-products of microbial growth potentially can be present in kerosene and result in corrosion of metallic systems contacting kerosene (see Sects. 5.4, 5.8 and 5.9). Small amounts of such contaminants as sodium and potassium in kerosene can cause corrosion in the turbine section of the engine. Particulates and microbes can plug fuel filters, screens, sump drains, valves, pipelines and increase fuel pump wear with potentially catastrophic results. Kerosene delivered to aircraft must be free from most corrosive compounds and other contaminants (vital requirement). Fuel kerosene cleanliness means the absence of solid particulates (mostly, rust and

Table 1.1 Content of sulphur in fuels according to the European standard requirements

Standard	Time of beginning of the standard to work	Sulphur content, ppm	
		Gasoline	Diesel fuel
Euro 1	1994 (October)	1000	2000
Euro 2	1999 (October)	500	500
Euro 3	2000 (January)	150	350
Euro 4	2005 (January)	50	50
Euro 5	2009 (January)	10	10
Euro 6	2014 (September)	10	10

Euro 1 (etc.) is the European standard requirements defining the acceptable limits for exhaust emissions of new vehicles sold in European member states (and sulphur content in gasoline and diesel fuel appropriately)

dirt), free water, and microorganisms. Kerosene may contain different additives (up to 0.1 %) for improving its properties (see Sect. 2).

Gas oil (diesel fuel, diesel oil, petrodiesel, heating oil) is a mixture of different hydrocarbons boiling at 180–370 °C. The carbon numbers range from 12 to 24 (see Appendix A). Gas oil is composed of about 50–80 % paraffins (including normal, iso, and cycloparaffins), and 20–50 % aromatic hydrocarbons (including naphthalenes and alkylbenzens). Gas oil may be produced by the Fischer-Tropsch synthesis, and by hydrogenation of biodiesel (see Sect. 4.2). Gas oil used in heating systems is also called heating oil. The difference is that the requirements for diesel fuel (gas oil) used in vehicles need significantly lower amount of sulphur and better cleanliness than that in gas oil which is intended for heating systems. ‘Pure’ gas oil is not corrosive. The presence of sulphur and its compounds (especially H₂S) explains corrosiveness of gas oil. Requirements to diminish amount of sulphur oxides in exhaust gases led to constraints of concentrations of sulphur not more than 10 ppm in diesel fuel intended for vehicles (Table 1.1). Allowable concentration of sulphur in gas oil intended for heating systems is 1,000 ppm. Microorganisms can proliferate in gas oil tanks’ bottoms in the presence of water and cause deterioration of gas oil, blocking of filters, and corrosion (see Sects. 5.4, 5.8 and 5.9). Requirements for concentrations of water are not more than 200 ppm in diesel fuel and 500 ppm in gas oil. Gas oil produced in distillation column at the oil refineries is very hot (~350 °C) and is transported in pipes needed special thermal insulation. This situation can result in corrosion under thermal insulation (see Sect. 5.9).

Fuel oil is a fraction obtained from distillation of crude oil, either as a distillate or a residue.

Fuel oil consists of long hydrocarbon chains, particularly alkanes, cycloalkanes, and aromatics. The boiling point and carbon chain length of the fuel oil increases with its grade number (see Appendix A, Table A.10). Fuel oil is a viscous organic material containing many heavy hydrocarbons and is a liquid at T > 90 °C. Therefore tanks containing fuel oils are furnished with heating coils with hot steam which are set at the height of the first strip (~0.5–1 m height from the bottom) in the tanks in order to store and then to transfer the fuel oil in liquid state.

Fuel oil is burned in furnaces or boilers for the generation of heat or used in engines for the generation of power. Liquid fuel oil is transported through pipelines and the temperature of metal surface is $\sim 90^{\circ}\text{C}$. This situation requires special coatings (resistant to high temperatures) and sometimes thermal insulation. Thus corrosion may occur under thermal insulation (see Sect. 5.9).

Asphalt (bitumen, refined bitumen, asphaltic bitumen, pitch) is the residual fraction obtained by distillation of crude oil. It is the heaviest fraction with the highest boiling point ($> 525^{\circ}\text{C}$). Asphalt is usually stored and transported at $\sim 150^{\circ}\text{C}$, as at lower temperature it will solidify. Therefore storage tanks containing asphalt are furnished with thermal insulation. Such situation can result in corrosion of external surfaces of tank walls and pipes under thermal insulation (see Sect. 5.9). Asphalt softens when heated and is elastic under certain conditions.

In addition to conventional (traditional) fuels described above, *oxygenates*, *aromatics (BTX)*, and *biofuels* also are used separately or in mixtures with conventional fuels. Aromatics (up to 35% vol.) are formed in gasoline as a result of processing at oil refineries' units. Oxygenates are added to gasoline instead tetraethyl-lead in order to increase its octane number and better burning of gasoline (see Sects. 2.3 and 3). Their properties and aggressiveness to metals, alloys and polymers will be described in appropriate sections.

1.2.1 Corrosiveness of Petroleum Products

Petroleum products consist of hydrocarbons that are not corrosive to metals and alloys.

However, dissolved water and oxygen, hydrogen sulphide, certain organic sulphur- and oxygen-containing compounds in petroleum products can cause corrosion. This corrosiveness may be further compounded by the proliferation of microorganisms in the presence of water.

Corrosion of metals occurs owing to the presence of water and oxygen in the environment (which includes fuels). Oxygen dissolved in petroleum products can also cause oxidation of hydrocarbons and formation of corrosive compounds on one hand and degradation of fuels on the other hand.

Note that oxygen-containing compounds can influence corrosivity of petroleum products. In contrast to sulphur- and nitrogen-containing compounds that their amounts in petroleum products depend on their quantities in original crudes, oxygen-containing compounds not only pass from crudes into petroleum products but also are formed as a result of oxidation of unstable (predominantly unsaturated) hydrocarbons containing in petroleum products during their storage, transportation, and use. For instance, many unstable hydrocarbons (mainly alkenes) appear in kerosene due to thermal cracking, and, as a result of oxidation, may be formed oxygen-containing compounds. The amount of oxygen-containing compounds in petroleum products depends on composition of petroleum products and oxidation conditions. This process occurs in large amounts of liquid petroleum products at temperatures

between -50 and $+50^{\circ}\text{C}$ and depends on the diffusion rate of the molecular oxygen in the organic phase. The oxidation rate of petroleum products increases at the beginning of their storage. After their saturation by formed oxygen compounds, some oxygen-containing compounds inhibit further oxidation, which decreases to zero. Corrosion products (rust) on the inner surfaces of carbon steel tanks and pipelines can work as hydrocarbon oxidation catalyst. Storage and transportation of petroleum products in an inert atmosphere (nitrogen) or isolated from atmospheric oxygen would restrict or prevent their oxidation. Ensuring such conditions, however, is difficult, so oxidation of unstable hydrocarbons in petroleum products is inevitable.

Water and oxygen dissolve in petroleum products after distillation and treatment in oil refinery units during production, transportation, storage, distribution, and further use of fuels. Many naval vessels (tankers) use compensated fuel ballast systems. These systems help maintain the vessel's stability by replacing consumed fuel with seawater. This method exposes the fuel tank to marine microorganisms and salts (mainly chlorides), leading to accelerated corrosion and fuel degradation.

In spite of the requirements to restricted sulphur concentration in fuels regularly become more and more strictly, not all substances containing sulphur are removed from fuels (see Table 1.1).

Light organic acids (formic HCOOH and acetic CH_3COOH) and chlorides can be in petroleum products and in the presence of water are corrosive to metals.

When olefins (unsaturated hydrocarbons) are contained in petroleum products they are easily oxidized by dissolved oxygen to hydroperoxides and peroxides which increase corrosiveness and aggressiveness of petroleum products to metals and polymeric materials. This oxidation is accelerated by certain dissolved metals, especially copper. Hydroperoxides and peroxides can turn into organic acids. Saturated hydrocarbons (alkanes and cycloalkanes) are oxidized slowly with the formation of hydroperoxides which are corrosive by themselves as well they turn into alcohols (ROH), aldehydes (RCHO), ketones (RCOR_1), organic acids (RCOOH), and then into esters (RCOOR_1) and ethers (ROR_1). Some of them can be aggressive to polymers and organic coatings. Corrosion of bronze in jet fuel under water condensation can be enhanced by mercaptans and by products of the oxidation of the fuel.

Oxygenated fuels usually containing either methyl tertiary-butyl ether (MTBE) or alcohols (methanol and ethanol) (see Sect. 3) can increase their corrosiveness to metals and aggressiveness to polymers and organic coatings.

Dissolution of atmospheric oxygen in petroleum products is the first stage of further corrosion and oxidation of hydrocarbon components. Thus the two main "actors", water and oxygen, are dissolving in enough quantities in petroleum products and their components are responsible for electrochemical corrosion to occur. Therefore solubility of water and oxygen in petroleum products is critical for occurring corrosion and will be described separately.

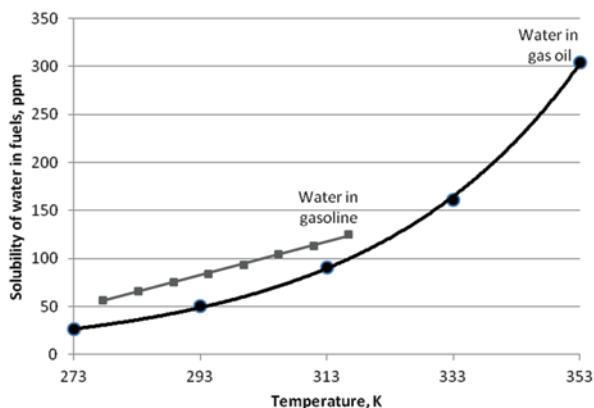
1.2.1.1 Solubility of Water in Petroleum Products

Water in petroleum products comes from a number of sources. Many oil refining processes employ steam and water, either directly or as heat exchanger coolant. Any water picked up during processing is removed before the fuels leave the oil refinery. Petroleum products can absorb water from the air by different ways: during transportation, storage in tanks, and distribution. The amount of water depends on the relative humidity and the temperature of the air. The more humid the air, the greater amount of the water vapor will dissolve in petroleum products. Water vapor can condense directly from the air into petroleum products. Because most pipelines are buried, petroleum products can cool during transmission. Cooling causes droplets of free water to form if fuels were close to be saturated with water when they were injected into the pipeline. Even if the fuel was dry on injection, it may pick up free water deposited in low spots in the pipeline. Rain water may leak by the seals in storage tanks containing floating roofs. Water vapor in moist air may condense in fixed-roof storage tanks, which must be vented. Air containing water vapor flows in and containing hydrocarbon vapors out of fixed-roof tank as petroleum product is pumped in or pumped out. When air containing water vapor is cooled at night in the tank, water may condense in the fuels. When fuels are saturated by water they are in equilibrium with free water or moist air. Usually fuels which are close to an interface with water (or air) reach equilibrium with water in several minutes. However, in large storage tanks some amounts of the fuels are arranged in large distance from the interface. In the absence of mixing, it will take a lot longer time for this portion to reach equilibrium with water. In fact, fuels in large tanks may never come to complete equilibrium with water since ambient temperature and relative humidity are constantly changing.

Sometimes water vapor in the air do not cause enough amount formation of liquid water for phase separation. In any case, even in “hermetically” closed from the atmosphere tanks or pipelines water can appear. Water in fuels may be either fresh or containing dissolved salts and other electrolytes. Temperature drop under the dew point causes liquid water formation. This water usually is formed on the surface of metallic equipment and results in corrosion. Water in the fuel also can cause erroneous readings on the aircraft’s fuel quantity gages, which can be exceedingly dangerous in flights. In spite of requirements of all standards for fuels that fuels must be free of water, water can occur in three different forms in fuels: dissolved in the fuel; as a fuel-water emulsion; and as a separate phase (free or undissolved water).

Dissolved Water in Fuels Dissolved water is water absorbed in the fuel, namely, water molecules are distributed between molecules of hydrocarbons. Fuels in contact with free water are saturated with water, namely, hydrocarbons containing in fuels dissolve all the water they can hold. This maximum concentration of water (named saturated) in the fuel where adding more water does not increase its concentration in the solution is called *solubility*. This is thermodynamic value of equilibrium concentration and concerns solubility of any substance in solvent.

Fig. 1.1 Solubility of water in gasoline and gas oil versus temperature [6]



The Karl–Fischer method is used for the determination of water concentration in crude oil and petroleum products [2–4]. Water molecules are polar molecules while petroleum products are made up from non-polar hydrocarbon molecules. They cannot interact through the same intermolecular forces and therefore water is very slightly soluble in petroleum products varying from about 30–400 ppm (see Appendix D). The standard ASTM D975-11 for diesel fuel (gas oil) allows up to 500 ppm water which includes both dissolved and free water [5]. Usually some amounts (~30–80 ppm at 20 °C) of dissolved water are present in all petroleum products.

In addition to temperature and relative humidity of air with which fuels contact, solubility of water in fuels depends mainly on fuel composition. Solubility of water increases in the row: alkanes < cycloalkanes < alkenes (olefins) < aromatics. The higher molecular mass of alkanes and less the temperature of the fuel the less water solubility (Fig. 1.1). Therefore solubility of water in gasoline greater than in gas oil. Increase of the temperature from 273 to 313 K causes three times increase of solubility of water in gas oil.

Water solubility in fuels is greatly influenced by the presence and concentration of aromatic and olefin compounds. Appearing aromatic polar molecules in petroleum products cause increasing of solubility of water. Aromatics dissolve 5 to 10 times more water than saturated hydrocarbons of the same carbon number of atoms (see Appendix D). This is the cause that the maximum amounts of aromatics and olefins permitted in kerosene (jet fuels) are 25 and 5% vol. respectively.

To sum up, solubility of water changes with the variation day—night, period of a year, climatic zone, relative humidity, and for aviation fuels, altitude of flight. Dissolved water cannot be detected by eye or chemical reaction, and cannot be removed by settling or filtration. Fuel containing dissolved water will appear ‘clear and bright’.

If the temperature of fuel saturated with water decreases, some of the water dissolved in the fuel will turn into many very small droplets distributed throughout the fuel called *emulsion*.

Emulsion Water-in-Fuel An emulsion is a mixture of two or more liquids that are usually immiscible (unblendable). Emulsions are part of a more general class of two-phase systems of matter called *colloids*. We know and use emulsions from our childhood: milk, mayonnaise, creams, and vinaigrette. Milk is an emulsion of milk fat (saturated fatty acids triglycerides) and water. Even the word *emulsion* means *to milk* (from the Latin). Thus, in emulsions, very small droplets of one liquid (the dispersed phase) are dispersed in the other liquid (the continuous phase). The boundary between these phases is called interface. The emulsion water-in-fuels represents finely divided drops of water in fuels. Cloudy (hazy, milky) appearance in fuels usually indicates water-in-fuel emulsion. This occurs because the many phase interfaces scatter light as it passes through the emulsion. The suspended droplets give the fuel a cloudy appearance. The haze will disappear if the fuel is warmed enough to redissolve the water.

While immiscible liquids normally separate if they have different densities or surface tensions, an emulsion can persist for a long time. At $T < 0^{\circ}\text{C}$, water drops in such emulsion freeze in the form of thin spindle- and needle-shaped ice crystals which are arranged not only in the volume and upper part of the fuel, but also on the inner surface of metallic tanks as its temperature is lower than that of the fuel. Most emulsions are inherently unstable (it is better to say metastable). They may be stabilized by *emulsifier* (called also *emulgent*, *surfactant* or *detergent*) that congregate at the surface of the droplets, preventing them from coalescing. *Surfactants* (*surface active agents*) are substances that are active at the surface between the immiscible liquids, namely, cause a marked reduction in the interfacial tension of liquids and thus cause the fuel and water to mix more easily and form very stable emulsion. Because surfactants work at the interface, not in the bulk liquid, their small amounts can affect the properties of a large volume of liquid fuel. Some surfactants can be present as naturally occurring substances in crude oils, such as *naphthenic acids* and *phenols*. Others (*sulfonic acids*, *sulfonates* and *sodium naphthenates*) may be formed in the oil refining processes. Typical surfactants are shown in Appendix A (Table A.6). Surfactants are commonly removed from kerosene by passing it through clay (clay treating) in the oil refineries. *Surfactants* may be *detergents*, cleaning compounds (soap) used to clean fuel storage tanks and earner vehicles, *greases* used to lubricate valves, and *corrosion inhibitors* used in fuels to prevent or reduce corrosion in pipelines and tanks.

Surfactants in jet fuel can be a major problem. These substances accumulate in the coalescer elements of filter/separators (devices for separation of emulsion water-jet fuel), because they, like water, are attracted to and stick to the hydrophilic surfaces of the coalescing medium, and thus destroying the ability of the elements to coalesce and remove water from jet fuel.

Free Water in Fuels Free water exists as a separate liquid phase in fuels and may be in droplets (seen by naked eyes) or in gross amounts (layers) in the bottom of

a tank or any container (as most fuels are lighter than water). If fuel and water are mixed, the droplets coalesce slowly because of their small size, and at last they will separate again.

Dissolved water in fuels as a rule does not cause a corrosion problem. Water-fuel emulsion and free water are potentially corrosive in fuel systems. Dissolved water, however, may also be a problem in the sense because it can become free water as water-saturated fuel is cooled. For instance, when the temperature of the airplane with the tank containing 9,000 l of jet fuel decreases from 15 to 0 °C, 400 g of liquid water can be separated from the fuel. Thus, solubility of water in jet fuel is 56 ppm, and after separation, thin layer of water of 15 μ of thickness can be formed on inner surface of the tank, or 53,237 layers of water molecules. If all water is separated only on the bottom of the tank with the area of 6 m², about 200,000 layers of water molecules are separated on the bottom surface.

Free water is a critical contaminant in fuels because it plays a major role in corrosion and in microbiological growth, deterioration of fuels and further MIC occurring. In addition, water in jet fuels can be a serious hazard since it can freeze out in the fuels system and result in mechanical difficulties in the engine, fuel lines, filters, and in other locations of the aircraft. Free water is usually removed by a filter separator. Another important participant in corrosion of metals in fuels is dissolved oxygen.

1.2.1.2 Solubility of Oxygen in Fuels

When fuels contact air, its gaseous components (oxygen, nitrogen, carbon dioxide, inert gases, and water vapor) partly dissolve in fuels. Non-polar oxygen molecules dissolve well in non-polar hydrocarbons and are transported on large distances by diffusion or convection during various processes of aeration: transportation, pumping over, pouring out, filling, emptying, filtration, and storage of fuels. Experimental data of solubility of oxygen in liquid petroleum products, fuels, alcohols, bio-fuels, their components, and, for comparison, in water are given in Appendix E. It is very important to mention that oxygen dissolved in fuels is spent on two main processes occurring inside of liquid media: oxidation of unstable hydrocarbon components and corrosion of metals. Both processes are limited by diffusion of oxygen in fuels. This means that the rate of both oxidation processes is greater than the rate of diffusion of oxygen, and as a result the concentration of dissolved oxygen in fuels will increase and reach its maximum value called *solubility*. Solubility is a limited, maximum, equilibrium concentration of dissolved oxygen in a liquid which contacts molecular oxygen in gaseous phase:



We will describe some main points of solubility oxygen data in pure hydrocarbons and their mixtures (fuels) (see Appendix E). The main gases of the air, nitrogen

(78.09% vol.) and oxygen (20.95% vol.) dissolve in fuels to saturated conditions, namely, to equilibrium concentration described by (1.8).

- a. Solubility of oxygen depends on temperature, pressure and the fuel type.
- b. Usually solubility of oxygen decreases with increase of density, molecular weight and boiling point of hydrocarbons. Solubility of oxygen in liquid hydrocarbons and fuels is greater 10–100 times than in water at the same temperature. The solubility of oxygen may be ranged: gasoline (naphtha) > kerosene (jet fuel) > gas oil (diesel fuel) > fuel oil; and hydrocarbons > alcohols > biofuels >> water.
- c. Solubility of oxygen increases with increase of its partial pressure, and decreases with increase of temperature.
- d. Solubility of oxygen in fuels is significantly greater (60–70%) than that of nitrogen. Therefore if volume ratio of nitrogen and oxygen in the air equals to 3.73:1, that in fuels equals to 2.07:1.
- e. If the fuel is saturated by one gas, another gas can not dissolve in it. This is very important point because if to saturate the fuel by an inert gas (nitrogen), it is possible to prevent dissolution of oxygen in the fuel and thus to prevent corrosion of metallic construction and auto-oxidation of the fuel.

Maximum concentration of dissolved oxygen in fuels occurs after their filtration. During filtration, area of liquid fuels contacting with air increases significantly. As a result of filtration, both processes, dissolution of oxygen and aeration of fuels, increase. As the presence of dissolved oxygen in fuels is critical for corrosion, like in water, various methods of removal of oxygen from fuels were developed.

- a. Treating of fuels by solid sulfite salts. They are oxidized by dissolved oxygen forming sulfate salts.



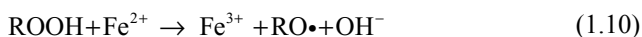
- b. Purging by inert gas (nitrogen).
- c. Vacuum degassing.

However, these methods are not used because of large amounts of fuels needed for treating.

System fuel—water—oxygen—nitrogen exists in continuously changing variable dynamic equilibrium which is difficult to regulate till the fuel will be isolated from ambient air. It is nearly impossible fully isolate fuels from the environment during production, transportation, storage and use of huge amounts of fuels. Therefore corrosion with the participation of dissolved oxygen is inevitable and we should use methods of monitoring and control of corrosion of different metallic constructions contacting fuels. Oxygen dissolved in fuels can oxidize certain organic compounds containing in fuels and increase their aggressiveness to metals and polymeric materials.

Formation of Aggressive Compounds to Metals and Polymers As a Result of Oxidation of Hydrocarbons Containing in Fuels The amount of unsaturated hydrocarbons (olefins), alkyl aromatic hydrocarbons, alkadiens and alkene aromatic

hydrocarbons in some fuels is not large but they are easily oxidized by dissolved molecular oxygen (O_2) at ambient temperatures. This process is called *auto-oxidation* which takes place intensively enough under conditions of transportation and storage of fuels. This occurs mainly in kerosene (jet fuel) and gasoline. As a result of *auto-oxidation* of certain organic compounds hydroperoxides (ROOH) are formed. Hydroperoxides are relatively stable intermediate compounds and can exist some short period. However, hydroperoxides are significantly more reactive than oxygen because energy bond O–O in ROOH three times wicker than that O=O in O_2 . Hydroperoxides break-up into radicals ($ROO\cdot$) which are very active chemical particles. They by themselves are aggressive to metals and polymers. The ending product of oxidation of hydrocarbons by hydroperoxides are organic oxygen-containing compounds, namely, alcohols, ketones, aldehydes, and organic carboxylic acids which are fairly enough stable during long storage of fuels. Increase of temperature causes the raise of the break-up rate of hydroperoxides. One of the break-up products of hydroperoxides is water. Therefore water in fuels can appear not only from water vapor containing in the atmosphere but also as a result of the break-up of hydroperoxides. Low molecular weight organic acids (e.g., formic and acetic acids) are dissolved well in water containing in fuels and corrosivity of such fuels can increase. Part of alcohols can react with organic acids with formation of ethers. In addition to organic acids, oxyacids and hydrogen peroxide (H_2O_2) also can be formed. They are also aggressive to metals and polymers. Breaking-up of hydroperoxides is accelerated by increase of temperature and presence of certain ions of metals, such as copper, iron (mainly Fe^{2+} and iron oxides), cobalt, manganese, tin, and by acidic compounds accumulating in fuels.



Thus breaking-up of hydroperoxides ROOH by ions Fe^{2+} results in formation of Fe^{3+} and formation of radicals $RO\cdot$ which favour further oxidation of hydrocarbons and formation of organic corrosive compounds containing oxygen atoms. Ferric ions Fe^{3+} play the role of cathodic depolarizer (receiver of electrons) which takes part on oxidation of pure iron



and thus accelerate corrosion. Ferrous ions Fe^{2+} appearing in process (1.11) take part in new break-up of hydroperoxides (1.10). Thus corrosion products of carbon steel, ions Fe^{2+} , take part in autocatalytic process.

When unsaturated hydrocarbons are finished in auto-oxidation during storage of fuels, saturated hydrocarbons can be involved in auto-oxidation. Alcohols, sulphur-, nitrogen- and oxygen-containing organic compounds can inhibit oxidation of hydrocarbons. Hydroperoxides are so good oxidizers that they can oxidize not only hydrocarbons but also organic sulphur- and certain nitrogen-containing compounds. For instance, organic sulphur-containing compounds can be oxidized to sulphonic acids which also are corrosive to metals.

It is wrong to think that only aggressive compounds are formed as a result of oxidation of hydrocarbons. Neutral compounds and even corrosion inhibitors of metals also can be formed. It is important to emphasize that some organic carboxylic acids can play the role of corrosion inhibitors. They can react with metals with formation of passive protective layers on metallic surface. Another function of certain organic oxygen-containing compounds formed in fuels is that they can form with water stable emulsions.

Definition of Corrosiveness of Petroleum Products Usually corrosiveness of media is defined by immersion of metal sample in it during some reasonable period and calculation difference in weight of the sample before and after immersion. Owing to complicated content of petroleum products where main corrosive factors are the presence of sulphur- and oxygen-containing compounds, solubility of water and atmospheric oxygen, it is not easy to define corrosiveness of fuels. Copper and silver are most susceptible to corrosion by sulphur compounds containing in fuels (see Eqs. 5.7 and 5.8). Therefore, the copper and silver strip corrosion test gives an indication of the presence of certain corrosive substances such as sulphur or acidic compounds that may corrode metallic equipment. This standardized test is a qualitative criterion and assesses the relative degree of corrosivity of fuels [7–9]. The test consists of placing a clean, polished copper or silver strip into 100 ml of the fuel for some period (usually 1 or 3 h) at certain temperature. The strip is removed and compared against a color chart standard that has four (for copper) and five (for silver) degrees of color. If the strip shows no indication of corrosion (the color of strip does not change) the test result is number 1 (for copper) or 0 (for silver). High concentrations of corrosive compounds causes tarnishing and blackening as a result generate number 4 or 5. This test detects the compounds that could corrode copper and silver systems contacting fuels. In the past silver strip test was used in British standard [10] for determination of corrosiveness of kerosene because some details in the Concord aircraft were made of silver. Silver is more susceptible to corrosion by sulphur compounds than copper. It is recommended to take off silver jewelry when taking water baths containing H_2S . Nowadays there are no silver materials in aircraft systems though silver alloys are used in fuel gauges in tank sender units and in automotive spark-ignition engines. Therefore silver strip test is used for the determination of the corrosiveness of gasoline [11, 12].

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Chapter 2

Fuel Additives

All good things come in small packages.

The Russian proverb.

Abstract Most fuels such as gasoline, kerosene (jet fuel), gas oil (diesel fuel) and fuel oil have drawbacks which do not allow their long term storage, make difficult transportation and even use. About 20 properties of fuels can be improved, maintained or imparted new beneficial characteristics by the adding of small amounts of certain chemicals named *fuel additives*. Fuel additives are added in very small concentrations: from several ppm to several thousands ppm. It is important that additives which improve some properties should not deteriorate other properties of fuels and its quality in general. Fuel additives are organic substances soluble in fuels: antifoams, anti-icing additives, anti-knock additives, antioxidants, antistatic additives, anti-valve seat recession additives, biocides, cetane improvers, combustion chamber deposit modifiers, corrosion inhibitors, demulsifiers, deposit control additives, detergents, diesel fuel stabilizers, drag reducing agents, dyes and markers, leak detector additives, lubricity improvers, metal deactivators, and wax anti-settling additives. Additives to fuel oil also are described: demulsifiers, sludge dispersants, combustion improvers, and additives for prevention oil-ash and cold-end corrosion in boilers. Action of fuel additives, their application, risks and benefits are analysed.

Most fuels such as gasoline, kerosene (jet fuel), gas oil (diesel fuel) and fuel oil have drawbacks which do not allow their long term storage, make difficult transportation and even use. For example, certain components of fuels can be oxidized and their properties can be deteriorated. In this case, antioxidants, stabilizers and metal deactivators are injected into fuels. Jet fuel can be frozen at low ($< -49^{\circ}\text{C}$) temperatures. In this case, wax anti-settling additives diminishing freezing temperature of jet fuel are needed. If dissolved water is present in jet fuel, water can be turned into ice at $T < 0^{\circ}\text{C}$, which can clog filters, and fuel will not flow into engine. Such situation can cause crashes of airplanes. Anti-icing additives are needed in such cases. Sometimes contact of gasoline and kerosene (containing corrosive substances water and oxygen) with metallic equipment may result in corrosion. In this case, corrosion inhibitors are required for injection into fuels. If water appears in jet fuel or gas oil, microorganisms can proliferate and result in biofouling, deterioration of fuel properties, clogging of filters, screens, sump drains, valves, pipes where fuel flows into engines, their malfunctioning and uncontrolled severe corrosion. In this case,

biocides are needed to be injected into fuels. Complex hardware in modern engines led to the need for additives in the gasoline to keep carburetors, intake valves, injectors, sensors, and the pollution control devices clean and working well.

About 20 properties of fuels can be improved, maintained or imparted new beneficial characteristics by the adding of small amounts of certain chemicals named *fuel additives*. Thus, in order to get better some properties of fuels during storage, transportation, distribution and use, different additives are injected into fuels.

It is important to mention that sometimes oxygenates (ethers and alcohols) which are added to gasoline in large amounts (up to 15 % vol.) are thought of as additives. They are not additives and are the competent components of gasoline (see Sect. 3).

Fuel additives are added in very small concentrations: from several ppm to several thousands ppm (1 ppm=0.0001 wt%). In such way, they are similar to corrosion inhibitors which also are added in small amounts in different media and significantly diminish their corrosivity. Usually such small amounts of additives are not reflective of the bulk composition of the mixture (fuels), but can significantly influence their properties. It is important that additives which improve some properties should not deteriorate other properties of fuels and its quality in general. Fuel additives are organic substances soluble in fuels (Appendix F). Some of these additives may help to maintain fuel quality (e.g., antioxidants, stabilizers, corrosion inhibitors, and biocides). Others may aid the movement of fuel through the distribution chain and into the vehicle tank (e.g., flow improvers, pipeline drag reducers, demulsifiers, and antifoams); may be added for legal reasons (e.g., dyes and markers) or can address specific concerns from motor manufactures (e.g., deposit control additives and lubricity improvers). We will describe fuel additives and how they work.

2.1 Action of Fuel Additives and Their Application

Use of gasoline fuel additives largely reflects developments in engines design and refinery operations, as well the problems occurring during storage and transportation of gasoline. Use of kerosene (jet fuel) additives reflects strict requirements to maintain properties of jet fuel. Use of diesel fuel additives reflects the impact of growing diesel fuel demand and the changing technology of diesel engines. Sometimes additives are divided according to the name of fuel: gasoline, jet fuel, diesel fuel and fuel oil additives. It is conditionally because the same additives (e.g., antioxidants and corrosion inhibitors) can be used in gasoline, jet fuel, and diesel fuel. Situation with aviation fuels (jet fuel and avgas) is unique in that only those additives specifically approved may be added to jet fuel. Before an additive can be approved for use in aviation fuel, it must undergo extensive testing to show both that it is effective and that it does no harm to any other fuel properties. To guard against harmful additive interactions, an additive must be tested at four times its maximum dosage in the presence of other additives before it is approved.

Antifoams All diesel fuels have a natural tendency to produce foam when pumped from a service tank into a vehicle's tank. This tendency is overcome by addition of polysilicone compounds.

Anti-icing additives Water in its liquid state is not only the cause of corrosion of metallic equipment and structures. In jet fuel or avgas, water turns into ice at temperatures below 0°C. Ice can form from dissolved water in fuel tanks at low temperatures during flights at high altitude. The freezing point of jet fuel is -47°C at pressure 1 atm. If free water is present in jet fuel, it will turn into ice at $T < 0^\circ\text{C}$ while the jet fuel is still liquid. The ice crystals can prevent fuel flow and possibly starve the engine for fuel. After the 1958 crash of a B-52 attributed to ice in the fuel, causing five of its eight engines to fail due to fuel starvation, anti-icing additives were introduced into military aviation fuels in the early 1960s.

To illustrate how the freezing point of water can be lowered, I describe three real-life incidents. In Siberia (Russia) in winter, where the air temperature was -45°C, I saw that car drivers did not use pure water for cooling their car engines. They added a solution called 'antifreeze', containing organic liquid alcohols—ethylene glycol or di-ethylene glycol—to their cars' cooling water in order to reduce the freezing point of the water used in their radiators. An 'antifreeze' is an additive (chemical compound) that lowers the freezing point of water. In Moscow's cold winters (the second example), I saw that table salt (NaCl) powder was dispersed on icy roads in order to lower the freezing point of water; namely, to turn ice into liquid water. Thus the ice combined with the salt turns into a liquid aqueous solution. The ice did not freeze at -5°C and even at -10°C to -15°C, and as a result, cars and people could move without danger of slipping, skidding, falling and accidents. The third example of use of de-icing solutions concerns flight in winter when the temperature is around 0°C. Once on a winter flight when I was inside the airplane, waiting to takeoff, I observed how de-icing (removal of snow, ice and frost from a surface) of both wings was done by spraying aircraft with a de-icing fluid. This fluid was based on propylene glycol, similar to ethylene glycol antifreeze used in some automobile engine coolants. Ethylene glycol is still in use for aircraft de-icing in some parts of the world because it has a lower operational use temperature than propylene glycol, but propylene glycol is more common because it is classified as non-toxic, unlike ethylene glycol. The de-icing solution not only de-iced the surface at the moment when it was applied, but also remained on the surface and continued to delay the reformation of ice for a certain period of time and prevents adhesion of ice. Hence, I was sure that our departure and flight would be safe. What is common between these three examples?

The freezing point of a solution is lower than that of a pure solvent. This phenomenon is based on thermodynamic properties of solutions. The decrease of a freezing temperature of a solution is proportional to the concentration of a solute (added substance) in a solution that is composed of ethylene glycol, propylene glycol or salt in an aqueous solution (2.1).

$$\Delta T_{\text{freez}} = T_{\text{freez}}^{\circ} - T_{\text{freez}} = i \cdot K \cdot m \quad (2.1)$$

where ΔT_{freez} is the decrease of freezing temperature of a solution; T_{freez}° and T_{freez} are the freezing temperature of pure solvent (water in this case) and solution respectively; i is a coefficient which shows electrolytic properties of a solute (how solute dissociates into ions in the solution), for instance, $i=1$ for non-electrolytes (ethylene glycol, propylene glycol and di-ethylene glycol among them), and $i=2$ for the table salt NaCl (if it fully dissociates into ions in water); K is the *cryoscopic* (*cryo* from the Latin means *cold*) constant which characterizes solvent (water in this case); m is the molality (concentration) of a solution (number of moles of a solute in 1 kg of a solvent).

According to (2.1) everyone can calculate the amount of a solute (for instance, ethylene glycol) in kilograms which must be added to water in order to diminish freezing point to any needed temperature. For instance, 3 kg of ethylene glycol must be added to 1 l of pure water in order that water will not turn into ice at -45°C . Certainly this solute must well dissolve in the solvent. Similar principle exists when anti-icing additives are injected into jet fuel, avgas or diesel fuel. They decrease the freezing point of dissolved water in the fuel. *Anti-icing additives*, or *icing inhibitors*, or *fuel system icing inhibitors* (FSII, pronounced “fizzy”) work by combining with water that forms solution and decreases the freezing of the aqueous solution so that no ice crystals are formed in the fuel. Anti-icing additives have hydroxyl groups (OH) in their structure which posses high affinity to water and long hydrocarbon chain for providing enough solubility in the fuel as well as prevention separation under temperature exploitation conditions. The first anti-icing additive in jet fuel was ethylene glycol (blue in color), but in the mid 1990s was changed to a clear di-ethylene glycol (exactly as in Siberia). The examples of FSII which are used today are di-ethylene glycol monomethyl ether (Di-EGME), ethylene glycol monomethyl ether (EGME) and isopropanol (IPA). Usually their concentrations are 1,000–2,000 ppm in fuels. These additives are slightly soluble in fuel but are very well soluble in water and its freezing point decreases to -60°C in the presence of additives. Anti-icing additives do not lower the freezing point of the fuel, only the water in the fuel. Unlike commercial and most Navy aircraft, Air Force aircraft do not have fuel heater systems to prevent moisture in the fuel from freezing. Water removes anti-icing additives from fuel, so introduction of water must be avoided. It is important to emphasize that the Di-EGME is also biocide and can be used for inhibiting microbiological growth in aircraft fuel systems, mostly *Cladosporium resinae* fungi and *Pseudomonas aureginosa* bacteria known as hydrocarbon utilizing microorganisms or *HUM bugs* (see Sect. 5.4). In fuels containing anti-icing additives, stagnant water bottoms can absorb large amounts of anti-icing additives. This aqueous solution with anti-icing additive can disarm water absorbing elements allowing water to pass down-stream. Therefore anti-icing additives are injected into jet fuel if it does not contain free water.

Anti-knock additives (Antiknocks) First, we will describe *knocking*. Normal combustion in a spark-ignition, internal combustion engine is initiated by a spark. The flame front fans out from the spark plug and travels across the combustion chamber rapidly and smoothly until almost all the fuel is consumed. *Knocking*, called also

detonation is the sound produced by abnormal combustion. Some of the unburned mixture components ignite spontaneously (auto ignites) and burns very rapidly. In other words, auto ignition is spontaneous ignition resulting in rapid reaction of the air-fuel mixture in an engine. The flame speed is many times greater than the normal ignition spark. In a reciprocating engine, the noise associated with auto ignition is called *knock*. *Knocking* due to auto ignition is also called *spark knock*. The resulting precipitous rise in cylinder pressure creates the characteristic *knocking* or *pinging sound*. Combustion is a very rapid series of chemical chain reactions between fuel vapors and oxygen. Factors that increase the rates of combustion reactions favor uncontrolled ignition (auto ignition) and knocking. These factors include higher temperatures, higher pressures, and more time after spark ignition. Anti-knock additives interrupt the chain reactions that lead to auto ignition (detonation). In order to evaluate the ability of gasoline to resist knocking as it burns in the combustion chamber *octane number (rating)* was suggested (see Sect. 10). Thus the *octane number* is an indication of gasoline quality, namely to “wait for the spark”. In the power stroke of a gasoline engine, the air and fuel is compressed by the piston before being lit by the spark plug, whereupon, it must burn smoothly. Hence, the gasoline must be capable of withstanding heat from the compression and radiation as the flame approaches, without spontaneously igniting. If the gasoline cannot withstand these effects, it explodes and this results in a characteristic ‘pinking’ or ‘knocking’ sound from the engine. This is very dangerous as these explosions can cause loss of power, blast metals from the piston crown, or at worst, result in total engine failure.

The octane number scale is defined by two pure chemical reference fuels: normal heptane (*n*-heptane) with an octane number of zero (bad knock), and iso-octane (2,2,4-trimethylpentane) with an octane number of 100 (minimal knock). The selection of *n*-heptane as the zero point of the scale was due to its availability in high purity. This scale is arbitrary and is similar to Celsius temperature scale where zero temperature equals to freezing point of pure water and 100 temperature value equals to boiling point of pure water at the outer pressure 1 atm. Then were found substances with octane number higher than 100 (benzene, toluene, xylene, methanol, ethanol, ethers). The octane number of a blend of two reference compounds, *n*-heptane and iso-octane, is equal to the volume percentage of iso-octane it contains. A gasoline with an octane number of 96 has the same knock as a mixture of 96% vol. iso-octane and 4% vol. *n*-heptane. A fuel with a high octane number exhibits better resistance to auto ignition. Typical octane values for gasoline used in passenger cars are between 80 and 100. Of course, engineers searched for additives to gasoline in order to increase its octane number. On the chemical language, these additives had to increase activation energy of combustion of gasoline mixture. Activation energy is the minimum applied energy required to start chemical reaction (initiate combustion in this particular case). Injection of anti-knock additives allowed increasing activation energy of combustion which occurred smoothly (without detonation). Anti-knock additives were introduced in the 1920s to provide the octane rating needed to enable vehicle designers to increase engine compression ratios to levels which gave acceptable efficiency and performance.

Wide spectrum of anti-knock additives exists:

- a. Oxygenates: ethers—methyl tertiary-butyl ether (MTBE), ethyl tertiary-butyl ether (ETBE), tertiary-amyl methyl ether (TAME), di-isopropyl ether (DIPE); alcohols—methanol, ethanol, tertiary butyl alcohol (TBA) (see Sect. 3). Really they are not additives but components of fuels, because are added in large amounts (3 % vol. methanol to 15 % vol. MTBE).
- b. Aromatic hydrocarbons (aromatics): toluene, xylene, and benzene. The latter is toxic (including carcinogenicity) and therefore its amount is restricted by 1 % vol. Maximum allowable concentration of aromatics in gasoline is 35 % vol. These compounds possess similar problems like alcohol fuels, as they “eat” elastomer fuel lines (see Sect. 6.2) and has no lubricating properties as standard gasoline does, and thus can break down fuel pumps and cause upper cylinder bore wear.
- c. Aromatic amines: m-toluidine, p-toluidine, p-tert-butylaniline, technical pseudocumidine, N-methylaniline, and cumidines. They were used in avgas during World War II.
- d. Organometallic compounds (carbonyls): methyl cyclopentadienyl *manganese* tricarbonyl, *iron* pentacarbonyl, and ferrocene (*iron* dicyclopentadienyl). Like the first anti-knock additive tetra-ethyl lead (TEL) is based on Pb, these additives also are based on metals Mn and Fe.

Each of them has benefits and disadvantages. Nowadays most spread anti-knock additives are oxygenates and aromatics (see Sect. 3).

Antioxidants (inhibitors of fuel oxidation) Gasoline, jet fuel and diesel fuel contain unstable unsaturated hydrocarbons (olefins and diens) which can polymerise and form gums. The gums are carried forward into the engine system, and can lead to its malfunctioning and breakdown. In addition, olefins and diens containing in gasoline react more readily with dissolved oxygen than the other classes of hydrocarbons. This is a paradox of our being, because life on Earth requires oxygen for its existence on the one hand, and from another hand oxygen is a highly reactive molecule that takes part in many unwanted processes. Oxygen oxidizes tissues of living organisms, metals, and fuels. The chain of oxidation reactions can result in formation of hydroperoxides (ROOH) and peroxides (ROOR') in fuels. They are highly oxidizing agents resulting in increase of corrosiveness of gasoline (see Sect. 1.2.1.2). Such problems (to stabilize the fuel and reduce the tendency for gum to form) can be avoided by injection of antioxidant chemicals. An antioxidant is a molecule that inhibits the oxidation of other molecules. A freshly-cut apple turns brown because of oxidation. If you spray lemon juice on exposed fruit or vegetable (e.g., avocado), these fruit and vegetable will not be oxidized because the lemon juice is an antioxidant.

Oxidation can produce free radicals which can start chain of oxidation reactions in fuels. Antioxidants work by interrupting this chain of reactions (removing free radical intermediates), preventing the formation of hydroperoxides, peroxides, soluble gums, or insoluble particulates. Antioxidants do this by being oxidized

themselves instead fuels. Antioxidants are often reducing agents, such as hindered phenols, aromatic amines and diamines, or mixtures of aromatic diamines (e.g., phenylenediamines) and alkyl phenols. Antioxidants became more important in the 1970s when increased the concentrations of olefin compounds in fuels. Antioxidants are the biggest gasoline additives. They are also used in aviation gasoline, jet fuel, diesel fuel, and biofuel (see Sect. 4). Prior to now antioxidants were injected as close as possible to producing of fuels at oil refineries. However, nowadays it is clear that nothing to hurry to inject them. It is possible to compare use of antioxidants in fuels with their function in living organisms (ascorbic acid or Vitamin C) and in corrosion of metals (corrosion inhibitors).

Antistatic additives When I was a child I saw many times how gasoline tankers moved on the road and metallic chain which was at the back of the tanker loudly drag along the asphalt. Why do gasoline tankers usually have metallic chains at the back? The metallic chain is supposed to get rid of any static electricity that builds up within the vehicle by directing it from the tankers into the ground or road. Preventing the buildup of static electricity excludes the possibility of a spark occurring if somebody happens to touch the unit. Gasoline is highly flammable, and its vapors are explosive, and the spark can provide an ignition source. When fuels (e.g., gasoline, jet fuel or diesel fuel) move through a pipe, hose, valve, filter, or storage tank, static electrical charge can be generated (see Sect. 5.3.1).

The Greek philosopher Thales of Miletus discovered about 2,500 years ago that, when rubbing fur against a piece of amber, a static force that would attract dust and other small particles to the amber was produced which now we know as the ‘electrostatic force’. The same phenomenon happens because two dissimilar surfaces (liquid fuel and solid surface of pipe or other object) move across each other and one of them (hydrocarbons containing in fuels) has very low electrical conductivity (non-conductors): 1–50 CU (conductivity unit) (see Sect. 5.3.1). When electrical conductivity of fuel is lower than 1 CU, it is practically does not charged. Such fuel is characterized by high purity but it is difficult to reach and keep. Thus, rapidly flowing liquid that is a relatively poor electrical conductor (like fuels) can result in a static charge being created much faster than it dissipates. The rate at which the static charge dissipates is proportional to the liquid’s ability to conduct electricity (electrical conductivity) (see Appendix F). When electrical conductivity of fuel is greater than 50 CU, static charge dissipates enough quickly, and electrical charge is not accumulated. Thus 50 CU is a minimum value in order to prevent accumulation of static electricity. When the accumulated charge exceeds the ionization electric potential (measured in volts) of the air above the liquid, it can discharge from the liquid surface as a spark. The energy of the spark can initiate an explosion if the liquid is flammable and the composition of vapor and air in the vicinity is in the flammable region. In order to prevent such explosions, three measures are used: earthing (bonding and grounding), pumping rate limits, and time for charge dissipation (relaxation time), before the fuel is exposed to air. Another measure is to inject some substances to fuels for increasing their electrical conductivity and charge dissipation. Therefore they are called *conductivity improving additives*, or

antistatic additives, or *static dissipater additives*, or *electrical-conductivity additives*. The chemicals used are fuel-soluble chromium substances, polymeric sulphur- and nitrogen-containing compounds, and quaternary ammonium salts. One of such additives, Stadis 450 (composed of 8 ingredients), is used at 3–5 ppm in jet fuel and avgas. When additives are used, the conductivity of the fuel must be between 50 and 450 CU. Use of antistatic additives reduces the hazard of electrical charge accumulation. These additives do not prevent charge generation; they increase the rate of charge dissipation by increasing conductivity of fuels. In other words, static dissipater additives aid in relaxing static charges and decrease the possibility of fires or explosions caused by static electricity. It is mistake to think that all additives (antistatic between them) have no deleterious effect. For instance, antistatic additive ASA-3 in concentrations 1–3 ppm has been used in jet fuel for many years. It comprised three compounds (chromium salt of an alkylated salicylic acid, calcium di (2-ethylhexyl) sulpho-succinate and organic polymer) which can serve also as a surfactant and a dirt disperser. Its use in combination with corrosion inhibitor revealed harmful effect on the coalescence ability of filter separator. Of course, its manufacture was stopped. Therefore it is important to examine all possible side-effects of new additives.

Anti-valve seat recession additives The lead additive (TEL), in addition to its primary purpose of increasing octane number, also provides a critical wear-reducing function by depositing a thin protective layer of lead salts on valve seat surface. Without this protection, exhaust valve seats wear or recede into the cylinder head. After banning of use of TEL in 1990s, the problem of wear appeared. The problem of valve seat recession is overcome by the use of chemicals based on potassium, phosphorous and manganese salts. The combusted metal salts act as a protective lubricant and prevent the direct metal-to-metal contact that would otherwise cause high wear.

Biocides (see Sects. 5.4 and 7.5) Most microorganisms which include bacteria and fungi (yeasts and molds) that live in the water ‘love’ hydrocarbons containing in kerosene (jet fuel) and diesel fuel. Thus liquid hydrocarbon fuels represent an excellent nutrient source. Microorganisms can be air or waterborne. Microorganisms ‘love’ heavy hydrocarbons (C_{16} and higher) containing in jet fuel and diesel fuel more than light hydrocarbons containing in gasoline and naphtha. When water appears in jet fuel or diesel fuel, the microbes begin to proliferate at the interface water-fuel. Detrimental action of microorganisms on fuels appears as deterioration of fuels, in biofouling, clogging of filters, and corrosion of metals contacting fuels. Certain fuel additives, especially those rich in nitrogen and phosphorous, encourage microbial growth. As a result the additives are degraded and their effect is lost. Biocides are substances that kill microorganisms. They also are called *antimicrobial agents*. Biocides are used in every aspect of life: from toiletries to air conditioners, drinking water and swimming pools. Certain sulphur organic compounds containing in conventional kerosene and diesel fuel are natural biocides. The desulfurization processes at the oil refineries make low sulphur kerosene and diesel fuel, and natural biocides are no longer present in enough quantities to kill microorganisms.

Biocides using in crude oil and fuels are organic substances composed of boron compounds (substituted dioxaborinanes), isothiazolines and ethylene glycol (injecting in fuels); 2-Bromo-2-nitropropane-1,3-diol, glutaraldehyde and heterocyclic compound based on thiadiazine-2-thione (injecting in aqueous phase contacting with fuels); some ethers and quaternary amines (injecting in diesel fuel). Since most biocides are toxic and dissolved in aqueous phase, any water bottoms that contain biocides must be disposed of appropriately.

Detrimental action of microorganisms on fuels appearing in biofouling, clogging of filters, deterioration of fuels, and corrosion of metals became beneficial when microorganisms are used in bioremediation. Bioremediation is the use of microorganisms to remove pollutants (in this case fuels are pollutants).

Cetane improvers The diesel engine does not contain a spark plug. It is a compression-ignition engine and relies on the diesel fuel to auto-ignite to begin combustion. The diesel fuel ignites after it is mixed with the hot air toward the end of the compression stroke of the engine. Ignition delay is the time between injection of the fuel into the cylinder and the onset of combustion. If the delay is too long, combustion is more violent (and hence noisier) and less efficient (causing high levels of exhaust emissions and poor fuel economy). This ignition delay is explained by the fact that there is no time for fuel to pass needed preparation for engine with ignition from compression. This preparation is accompanied by accumulation of peroxides which initiate auto-ignition. Thus intensity of oxidation, delay of ignition and the temperature of auto-ignition of diesel fuel depend on its chemical composition. Normal alkanes and alkenes are oxidized with large rate and at lower temperatures than aromatic hydrocarbons. Therefore the presence of normal alkanes and alkenes is desired as they provide shorter induction period during oxidation of fuels in the engine, and oxidation products (hydroperoxides) provide lower auto-ignition temperature, easy start and gentle work of the engine. In order to estimate an ability of diesel fuel to auto-ignite, we should choose two compounds: one of the best ability and another of the worst one to auto-ignite under compression. The first compound chosen is hydrocarbon alkane hexadecane ($C_{16}H_{34}$) named *n*-cetane, a liquid that ignites very easily under compression. It was given a base rating of 100. Another reference is alpha-methylnaphthalene ($C_{11}H_{10}$) with a value of 0. *Cetane number* represented the volume percent of *n*-cetane in alpha-methylnaphthalene that ignites similarly to the diesel fuel being measured. In 1962, because of difficulties in handling alpha-methylnaphthalene and its expense it was replaced with more stable compound heptamethylnonane (a C_{16} isomer isocetane). The latter was assigned a cetane rating of 15. *Cetane number* is the measure of how well diesel fuel ignites. Similar to the octane number rating that is applied to gasoline to rate its ignition stability, *cetane number* is the rating assigned to diesel fuel to rate its combustion quality. Engines operating on diesel fuels with a low cetane number are difficult to start, especially in cold weather, noisy, emit high levels of white smoke and hydrocarbon pollutants at start up, produce less power and consume more fuel. The greater amounts of alkanes, alkenes and naphthenes, and fewer amounts of aromatics are in diesel fuel the higher its cetane number. Diesel engines operate well with a cetane

numbers from 40 to 55. Not all diesel fuels have such values. In order to increase cetane number, namely, to initiate the oxidation of the fuel in the engine in liquid phase before the formation of vapor-air mixture and thus accelerate the formation of hydroperoxides and as a result to provide gentle, uniform and stable combustion in the engine, various additives are injected. These additives are alkyl nitrates (e.g., 2-ethyl-hexyl nitrate, octyl nitrate, iso-propyl nitrate, amyl nitrate) and di-tert-butyl peroxide. They initiate oxidation of cycloalkanes (naphthenes) and aromatics containing in large amounts in diesel fuels, breakdown during combustion to form free radicals, which increase the rate of decomposition of the hydrocarbon components of fuel, reduce ignition delay, and thus facilitate the start of engine.

Combustion chamber deposit modifiers All spark-ignited engines develop combustion chamber deposits. These deposits are formed as a result of condensation of partially-thermally oxidized hydrocarbons of gasoline and additive components on the relatively cool piston and cylinder head surfaces. Organic polyetheramines and compounds containing combination of a saturated carboxylic acid and an alkylated or alkoxyated amine are such additives for controlling (preventing or reducing) combustion chamber deposits in engines.

Corrosion inhibitors Corrosion of carbon steel tanks, pipes, and other equipment containing gasoline and naphtha occurs because of dissolved water and oxygen (see Sect. 5.3). Other aggressive compounds, such as elemental sulphur, hydrogen sulphide, mercaptans, disulphides, low molecular weight carboxylic acids and oxyacids can cause corrosion in diesel fuel and jet fuel. The more fuel is purified from corrosive sulphur- and oxygen- containing compounds and isolated from atmospheric oxygen and water vapor, the less its corrosivity. Free water appearing in fuels during their storage is especially corrosive because of organic low molecular weight corrosive compounds are dissolved well in this free water and become corrosive. Microorganisms also find favorable food and conditions for their proliferation at the interface water-fuel. Even if elemental sulphur, H_2S and mercaptans are absent in fuels, they may appear as a result of break-up of complicated organic sulphur-containing compounds. *Corrosion inhibitors are substances which are added in small amounts for decrease or prevention corrosion of metals.* High molecular weight carboxylic acids, aliphatic amines with long chains, the amine salts of carboxylic acids, aliphatic polyamines and polyamides are used as corrosion inhibitors of carbon steel in contact with fuels. These organic compounds are the polar molecules that adhere by the charged part to the metal surface and form the protective film which does not allow water, oxygen and other corrosive components reach the metal surface. In addition, carboxylic acids can react with iron and form nonsoluble salts on the carbon steel surface which also prevent the penetration of corrosive species and their further contact with the steel surface. Thus mechanism of protection may be adsorption or chemical reaction of inhibitors with metal surface. Corrosion inhibitors were introduced in 1940s and can be added to gasoline, jet fuel, and diesel fuel. Their concentrations are ranged between 5 to 100 ppm in gasoline, and 450 ppm in diesel fuel. Aliphatic amines are efficient corrosion inhibitors of carbon steel and copper alloys in both hydrocarbon and aqueous phases. Organic

sulphonates (dissolved in oil), other sulphur-, nitro-containing and amine-organic compounds are used in diesel fuels.

It is interesting to point out that certain carboxylic acids (e.g., acetic acid) can cause corrosion of metals while other carboxylic acids (e.g., dioleic acid) can be corrosion inhibitors.

We should emphasize that corrosion inhibitors play polyfunctional role as they prevent dissolution (corrosion!) of metals and thus prevent participation of metal ions (e.g., Fe^{2+} and Cu^{2+}) in oxidation of hydrocarbons in fuels. It is not recommended to inject corrosion inhibitors based on carboxylic acids into jet fuel pipelines because these acids remove deposits and clean inner surface of pipelines. As a result filters are blocked and periodicity of their change can be increased drastically, up to once per 3 days.

Demulsifiers (Fuel Dehazers) Water can exist in fuels in three forms: dissolved, emulsion, and free water (see Sect. 1.2.1.1). Finely divided water can create an undesirable haze and fuel-water emulsion. Haze in fuels can also be caused, stabilized, or exacerbated by fuel degradation products, wax, and inorganic contaminants. Haze can cause filter plugging, microbial activity, and corrosion, which must be resolved before the fuel can be shipped. Thus emulsions can deteriorate fuel quality. *Demulsifiers* (called also *fuel dehazers*) counter these effects preventing or removing haze from gasoline and diesel fuel. Demulsifiers include alkoxylated polyglycols and aryl sulphonates which are nonionic surfactants modifying the surface tension. In diesel fuel, they are used in combination with *detergents* (surface active agents). The coalescence of the water allows the water to separate from the fuel, gives a clear fuel and avoids the formation of an emulsion.

Deposit control additives (Dispersants, Cleanliness additives) One of main requirements of modern standards to the quality of fuels is absence of mechanical impurities and free water visible by naked eyes. Impurities with dimensions more than $5\text{ }\mu\text{m}$ are settled or removed by filters. Many particles of less than $5\text{ }\mu\text{m}$ exist in fuels and do not settle. In order to accelerate the aggregation of these impurities certain surfactants are added in very small amounts. Thus the aim of deposit control additives is to keep the whole fuel system completely clean and free of extraneous matter, namely, dispersants act to suspend any sediment particles from agglomeration. Amides, amines, amine carboxylates, polybutene succinimides, polyether amines, polyolefin amines, polymeric methacrylates and derivatives of 2-benzothiazole are used for this purpose. Additives that contain nitrogen or sulphur atoms are polar molecules and act as detergents, disperse deposit precursors and carry them forward in a very thin liquid film into the combustion chamber. As a result, fuel will be free from emulsion water, corrosion and wear products, resins, and soil dust. Deposit control additives must be liophilic (having affinity) to impurities and liophobic (no affinity) to hydrocarbons of fuels. Therefore they are poorly dissolved in fuels but prevent the formation of stable emulsions and suspensions. Many of these additives are used in combination with carrier fluids such as polyalphaolefins, polyethers, mineral oils, and esters. Use of these additives has profit for carburetors, gasoline port fuel injectors, diesel IDI (Indirect Injection) and DI (Direct Injection)

injectors, and inlet valves. Thus, deposit control additives help to maintain vehicle drive ability.

Diesel detergency additives (Detergents) Diesel fuels contain unstable compounds which can thermally degrade, and coke fouling can be formed in the annulus of the injector. Diesel fuel detergents help to prevent the formation of deposits on the injector nozzle partly by providing a film on the metal surface and partly by forming a protective coating around the developing deposit precursors. These detergents are succinimide and other ashless polymeric substances having some family similarity to the dispersants used in gasoline and automotive lubricants.

Diesel fuel stabilizers (Stability improvers) Diesel fuel can be stored for prolonged periods. This is particularly so for military use where it is of prime importance that the fuel remains fit for use throughout the storage period. If the fuel contains small amounts of olefins, nitrogen-containing compounds (not amines), organic acids, or dissolved metals, the fuel may degrade. Fuel can become dark, gummy deposits can form and may block filters. This problem can be mitigated by diesel fuel stabilizer additives which are long chain and cyclic amines.

Drag reducing agents Not at once crude oil and fuels were transported through pipelines. Crude oil was transported in old wooden whiskey barrels, which were made of standard capacity (~200 l). That's why we measure volume of crude oil in 'barrels' today. The first pipes were short to get crude oil from wells to nearby tanks or refineries. The rapid increase in demand for kerosene led to a need for its transportation for long distances. In the 1860s pipes began to be produced from carbon steel. When the fuel or crude oil pushes up against the inside wall of the pipe, the pipe pushes the liquid back down causing a swirling of turbulence to occur. Another problem is corrosion of inner surfaces of pipelines. When corrosion products appear and roughness increases on the inner surfaces of pipe, the operating pressure must be increased. If the wall thickness reduces as a result of corrosion, so does the maximum allowable operating pressure. If you continue to operate the pipeline at high pressures but the thickness has reduced, you risk a pipeline rupture. Therefore we have three choices for decision this problem: renew the pipeline, reduce the pressure and hence flow rate, or inject *drag reducing agents*. Injection of the latter allows for crude oil and fuel to be pumped through at lower pressures, saving energy. Therefore *drag reducing agents* are called also *drag reduction agents*, or *drag reducers*, or *anti-turbulent additives*, or *pipeline boosters*, or *flow improvers*. They are organic high molecular weight polymeric compounds that when injected into a pipeline (where the fluid is turbulent) can modify the flow regime by reducing the frictional pressure drop along the pipeline length. When the polymer is added, it interacts with the crude oil or fuel and the wall to help reduce the contact of the liquid with the wall. Drag reducing agents can reduce drag by up to 80% and can increase flow rates by more than 100%. Their use in pipelines can either provide an increase in flow (using the same amount of energy) resulting in a much higher throughput, or alternatively maintain the same flow rate whilst using considerably less energy. Following factors influence the efficiency of the drag reducing agents:

temperature, diameter of pipes, and roughness inside surface of the pipes. With a higher temperature, the drag reducing agent is easier to degrade. At a low temperature the drag reducing agent will tend to cluster together. This problem can be solved easier than degradation though, by adding another chemicals, such as aluminum stearate (or zinc, sodium and calcium stearates), to help lower the drag reducing agent's attraction to one another. Another factor is diameter of pipes. The less pipe diameter, the more drag reduction occurs. The rougher the inside, the higher the percent drag reduction occurring. Usually drag reducers are used in pipelines with flowing crude oil, diesel fuel, and gasoline.

Dyes and markers Fuel dyes are used in order to differentiate between various commercial types of fuels. For example, avgas 100LL (low lead) is colored blue, while avgas 100 is colored green. This is a safety measure to prevent misfueling of an aircraft. The dyes used have to be soluble in the fuels. Coloration of fuels is achieved by azo compounds ($R-N=N-R'$) and anthraquinone (aromatic organic compound). Red dyes are various diazo compounds. Anthraquinone dyes are used for green and blue shades. Dyes are used in gasoline, avgas, and diesel fuel. For instance, high-sulphur diesel fuel is colored red and low-sulphur diesel fuel undyed.

Leak Detector Additives Leak detector additives are used in order to detect and to locate leaks in fuel systems (especially in underground systems) or at our houses. Very-very small concentrations (several ppb; $1 \text{ ppb} = 10^{-7} \text{ mass \%}$) of odorants ethyl mercaptan ($\text{CH}_3\text{CH}_2\text{SH}$) or tetrahydrothiophene ($\text{CH}_2)_4\text{S}$) are added to the LPG composed mainly from propane-butane gas (we burn it in a stove at home) in order to detect a leak of the gas in the system according to specific unpleasant smell (like a skunk's ass) of the mercaptan. We can detect even 0.3 ppb *tert*-butyl mercaptan according to its odor in natural gas.

The only leak detector additive approved for aviation fuel is another sulphur compound, a gas sulphur hexafluoride (SF_6), that also can be detected at very low concentrations. Its presence is limited to 1 ppm. This gas, called 'tracer', is mixed with fuel as it is pumped through the distribution system. If any fuel leaks from the system, it will evolve the 'tracer' gas. Thus the presence of this gas outside of a fuel system is used to locate a leak. Infrared technology (hand-held device) is used for its detection.

Lubricity improvers (anti-wear additives) Lubricity is the 'smoothness' of the fuel, which affects wear and tear of moving metal surfaces in engine. The higher the lubricity, the easier a fuel can move through an engine, resulting in longer engine service. Diesel fuel injector pumps and jet fuel pumps often rely on the fuel itself to lubricate their moving parts. Until recently, the properties of the fuel are such that this has not been a problem. Organic sulphur- containing compounds present in fuels form film on metal surface. However, the advent of low ($<500 \text{ ppm}$) and ultra-low ($<10 \text{ ppm}$) sulphur diesel fuels in order to reduce exhaust emissions has changed the picture completely. Aromatics, sulphur-, oxygen- and nitrogen- containing polar compounds in the fuel act as natural lubricants. These helpful natural surfactants are removed by the refining processes used to produce the diesel fuel

qualities now required by most national and European specifications. The Euro 5 demand is 10 ppm of sulphur in diesel fuel (see Table 1.1). Thus improving the environmental conditions by the reduction of sulphur content in diesel fuel its lubricity properties were diminished. Non-polar hydrocarbons molecules do not possess by the protective properties similar to polar sulphur containing compounds which before were present in fuels. Lubricity additives solve the problem of poor lubricity of diesel fuels and jet fuels. These additives are surfactants, namely, long chain polar compounds (usually carboxylic acids) which give a mono-molecular layer on the moving metal surfaces, act as a boundary lubricant when two metal surfaces come in contact and protect against scuffing wear. Lubricity efficiency of polar functional groups in such media as octane can be arranged in following order: $\text{COOH} \approx \text{OH} > \text{NH}_2 \gg \text{S} \approx \text{COOR} > \text{Cl}$. Carboxylic acids are on the first place, alcohols and amines are close to the first. The molecules of surfactants are adsorbed on defects of metallic surface. Even the smoothest metallic surface has irregularities of 0.05–0.1 μm which is 1,000 times more than dimensions of surfactant molecules. Certainly the latter are adsorbed on such irregularities. Most anti-oxidants, corrosion inhibitors and additives increasing stability of fuels are surfactants, therefore they can play also the role of lubricity improvers. Thus carboxylic acids using as lubricity improvers are the same substances that are used as corrosion inhibitors. Both corrosion and lubricity are the surface phenomena. Therefore it is not too surprising that corrosion inhibitors also improve lubricity. Although the use of lubricity improvers in diesel fuels is relatively new, they have been used for many years in jet fuel which also gives pump lubricity problems.

Metal deactivators Some alloys containing iron, copper, zinc, chromium, and nickel can corrode during refining and transportation of different petroleum products with formation of hydrocarbon-soluble salts (naphthenates). These salts promote oxidation of some fuel components with subsequent gum formation and deposits in the fuel systems. For example, oxidation of olefins containing in petroleum products are accelerated by some dissolved metals, especially by copper ions. The function of metal deactivators is to prevent the oxidation of olefins, the formation of hydrocarbon-soluble salts and prevent degradation of fuel thermal stability. The most widely used chemical as the metal deactivator is N, N'-disalicylidene-1,2-propane diamine (Schiff base). Metal deactivators are chelating agents, namely, chemical compounds that form stable complexes with specific metal ions. The mechanism is to chelate (to form complex compound) dissolved metal ions, namely, to deactivate them in fuels. As metal deactivators "neutralize" activity of metal ions which initiate oxidation of olefins, they may be considered as antioxidants. This chemical also migrates to any metallic surfaces and inhibits the formation of soluble metal salts. Metal deactivators are used mainly in aviation gasoline and jet fuel.

Wax anti-settling additives (wax crystal modifiers) Crude oils contain normal paraffins (alkanes) in varying amounts. Diesel fuel contains 50–80% n-paraffins (C_{12} – C_{24}) (see Appendix A). In some respects these paraffins are very desirable in diesel fuel as they have a high cetane number and burn with low emissions.

When a diesel fuel is cooled, paraffins (which have higher freezing points than other hydrocarbons) are formed into the wax crystals in the fuel. Crystal formation in fuels begins from the appearing of tiny particles (less than 1 μm). Wax anti-settling additives prevent the formation of wax crystals, freezing temperature of diesel fuels diminishes to 20–50 °C, and thus improve the flow of diesel fuel at low temperatures. It is important to inject this additive before appearing of solid phase, namely, at enough positive temperatures. Wax anti-settling additives are polymeric materials (e.g., ethylene vinyl acetate co-polymers) which have high affinity to solid dispersed phase in diesel fuel and help to disrupt the wax crystal networks that form in diesel fuel as it cools. We should mention once more that the process that refineries use to remove sulphur from diesel fuel (see *lubricity improvers*) removes natural surfactants which previously were in conventional diesel fuels and raises the fuel cloud point (the temperature at which the paraffin in the fuel changes from a liquid to a solid wax). Thus unexpected problems with low and ultra-low sulphur diesel fuel gelling and plugging filters occur. In this case, the use of wax anti-settling additives is very important.

Reodorants In order to restore, enhance or disguise fuel's smell an odor reodorants are used.

2.2 Additives to Fuel Oils

Fuel oil is one of petroleum products (distillation fraction) obtaining in distillation of crude oils (see Appendix A). It contains many heavy hydrocarbons (asphaltenes among them), organic sulphur-containing compounds and some metals (vanadium, nickel, iron, sodium, and potassium). These components can cause different problems during transportation, storage and use of fuel oil. Fuel oil is burned in a furnace or boiler for the generation of heat or used in an engine for the generation of power. Therefore additives to fuel oil may be differentiated on those solving problems prior to combustion (transportation and storage) and during combustion.

Demulsifiers Presence of water in fuel oil can result in formation of stable emulsion, partly owing to the presence of naturally-occurring emulsion stabilizers asphaltenes (heterocyclic aromatic molecules) and naphthenic acids in fuel oil. Such emulsions are not simple to break into two phases, fuel oil and water. Situation is worsens if sea water is present in the emulsion appearing during marine transportation. Sea-water contamination can introduce sodium and other undesirable trace metals, chlorides and sulphates ions, thus presenting a major risk of high temperature corrosion to gas turbine hot section components. The gravity settling rate is hindered by the relatively high density of fuel oil. The separation of the emulsion water-fuel oil can be achieved by using either centrifugal or electrostatic separation equipment, plus the addition of demulsifiers. They are surfactants containing mixtures of alkyl-oxide copolymers and alkylphenol resins.

Sludge dispersants The presence of asphaltenes in fuel oil also can result in formation of suspension. During storage of such fuel oils in tanks heavy components containing asphaltenes and other suspended particulates are settled and aggregated at the bottoms. Then this sludge can enter through pumps to pipelines and can block them. Sludge dispersants (named also asphaltenes inhibitors) adsorb onto the destabilized colloidal asphaltene solid, dispersing it in the fuel oil phase. This prevents precipitation on tanks bottoms, pipe surfaces and other equipment.

2.3 Additives for Prevention Oil-ash and Cold-end Corrosion in Boilers

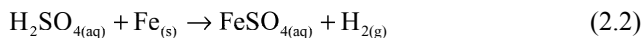
The main use of fuel oil is combustion in boilers. Combustion includes the reaction of oxygen with the basic chemical elements in fuel oil: carbon, hydrogen, and sulphur. Following main combustion products are formed: carbon dioxide (CO_2), water vapor (H_2O), carbon monoxide (CO), sulphur dioxide (SO_2), and sulphur trioxide (SO_3). Some components of fuel oil (vanadium, sodium, and potassium) can form solid oxides and salts (vanadates, sulphates, and pyrosulphates) named ash. Combustion may convert fuel components to any of the three states of matter: solid, liquid, or gas. In most combustion systems, the flue-gas temperatures can range from 1650°C in the flame to 120°C or less at the exhaust stack. When fuel oil containing vanadium, sodium, potassium and sulphur is burned oil-ash corrosion can occur in boilers ($T > 400^\circ\text{C}$) and cold-end corrosion in turbine blades and vanes ($T < 160^\circ\text{C}$).

Oil-ash corrosion Vanadium and sodium containing in the fuel oil are oxidized in the flame to V_2O_5 and Na_2O . Ash particles stick to metal surfaces, with Na_2O acting as a binding agent. Two oxides, V_2O_5 and Na_2O , react on the metal surface, forming compounds (vanadates) with a low melting point of about $510\text{--}870^\circ\text{C}$. These hot liquid compounds (named eutectics) fluxes iron oxide film (composed mostly from magnetite Fe_3O_4), exposing the underlying carbon steel surface to rapid oxidation. Thus *oil-ash corrosion* (named also *fire-side* or *vanadic corrosion*) occurs when fuel oil containing high amounts of vanadium, sodium and sulphur is used and then after combustion at $T > 510^\circ\text{C}$ molten slag composing from vanadium compounds forms on the tube wall. Additives based on magnesium compounds are injected into fuel oil in order to prevent oil-ash corrosion. Magnesium forms a complex with vanadium ($3\text{MgO} \cdot \text{V}_2\text{O}_5$, named magnesium orthovanadate) whose melting temperature 1243°C is significantly above that attained in most boilers. These additives also function as combustion catalyst to reduce particulate emissions.

During combustion of fuel oil, pyrosulphates ($\text{Na}_2\text{S}_2\text{O}_7$ and $\text{K}_2\text{S}_2\text{O}_7$) can be formed with the melting point less than 400°C . Corrosion mechanism is similar to that by liquid vanadates, namely, these molten slugs flux the protective iron oxide

film on the metal surface, exposing the metal beneath to accelerated oxidation. Additives based on magnesium, aluminum, and silicon are added in fuel oil in this case. The magnesium inhibition mechanism is based on formation of magnesium sulphate (MgSO_4) as an additional ash component. This compound is water-soluble and therefore facilitates the removal of combustion ash via periodic water washing of the hot gas path. Magnesium sulphate when hydrolyzed gives very acidic solution ($\text{pH} \sim 2$), therefore it is recommended to wash by aqueous soda solution. Additives containing silicon (Si) provide corrosion protection and improved ash friability.

Cold-end corrosion When combustion products cool on their way to the exhaust stack, gaseous products may condense, and liquids may turn to solids. The temperature at which sulfuric acid condenses (sulfuric acid dew point) varies from 116 to 166 °C or higher, depending on SO_3 and H_2O vapor concentrations in the flue gas. Cold-end corrosion occurs when the temperature of metal drops below the sulfuric acid dew point of the flue gas.



Economizers, air preheaters, induced-draft fans, flue-gas scrubbers, and stacks are prone to cold-end sulfuric acid dew point corrosion. In order to reduce or eliminate cold-end corrosion, it is recommended to use fuel oil with low sulphur and water content, and inject chemical additives based on magnesium and organo-metallic compounds. These additives prevent formation SO_3 during combustion of fuel oil.

2.3.1 Combustion Improvers

Most particulates emitted at exhaust stacks are generated during the combustion process and essentially result from incomplete burning of the hydrocarbons of the fuel oil. Minor contributions may also result from suspended solids in the fuel oil, particles ingested through the compressor air inlet filtration system, and other sources such as scale or ash in the engine and exhaust stack. Also, depending on dew point temperature conditions, H_2O and SO_3 formed during the combustion process may condense as sulfuric acid droplets and further increase the total amount of particulate measured. Incomplete combustion of fuel oil results in emissions of unburned carbon-rich particles. Aromatic fuel oils with long carbon chains are also well known for creating soot (unburned hydrocarbons). Smoke formation resulting from insufficient combustion is a very common problem in conventional steam boilers. In order to improve the combustion of fuel oils special additives are injected. They are iron-based catalysts that improve combustion efficiency by promoting the complete oxidation of heavy hydrocarbon components and carbon particles, thereby reducing soot and visible smoke emissions.

2.4 Risks and Benefits in the Use of Fuel Additives: The Environmental Balance

Environmental legislation has reinforced the need for detergents to keep the engine clean and maintain emissions performance long-term. The introduction of very low sulphur fuels led to a need for lubricity additives. Multifunctional additive packages may contain many of fuel additives in various combinations and solvent for package stability. Usually combination of antioxidants, dispersants, metal deactivators and stabilizers is used for control of diesel fuel stabilization. New additives must be chosen or created with exhaust catalyst compatibility. Additives are used also in oxygenated fuels and biofuels (see Sect. 4). There are no measurable effects of fuel additives on properties of polymeric materials. Additives are not used much in jet fuel and almost not at all in kerosene for heating or lighting.

Some fuel additives have two Janus faces, positive and negative. For instance, due to temperature or concentration changes the anti-icing additive Di-EGME comes out of solution either as the viscous ‘apple jelly’ or can appear as dirty brown concentrated liquid solution. This concentrated Di-EGME can cause corrosion of aluminum tanks and deteriorate tank linings. It can also corrode fuel controls and other fuel system components.

All fuel additives give benefits but we should pay attention that some of them are hazardous and toxic, namely fuel additives possess certain risk to man (dermal irritation and skin sensitization) and to the environment (ecotoxicity) from their use. Thus environmental balance between these two (risk and benefit) aspects is very important. More than half of the main classes of fuel additive components are not classified as dangerous; another 20% are classified as no more than irritant. It is noteworthy that solvents common to most fuel additive preparations are typically toxic or harmful to aquatic organisms and should be managed with the same care given to refined gasoline fractions in this regard. Typical concentrations of fuel additives are in the range 50–1,500 ppm and are very small relative to the consumption of fuels themselves. All fuel additives consist of carbon, hydrogen and oxygen atoms, with some other elements such as nitrogen. These additives are almost entirely consumed during the combustion and mainly form CO_2 and H_2O . Other gases, CO and NO_x are also expected, but fuel additive contributions to any unburned hydrocarbon emissions and particulates are negligible. Detergents also help to improve air quality by reducing CO , HC (hydrocarbons) and CO_2 emissions. Thus, fuel additives end their life as combustion products which are emitted to the environment.

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Chapter 3

Fuel Oxygenates

A little body often harbours a great soul

The proverb.

Abstract Anti-knock fuel additives based on metals (mostly tetra-ethyl lead) for increase the octane number of gasoline have disadvantages (in addition to toxicity of lead). Nowadays organic compounds (oxygenates and aromatic solvents) are used for increase the octane number of gasoline and its better burning. Their advantage is that they are fully burned and ash is not formed. The disadvantage of these organic compounds is that large quantities (to 15 % vol. oxygenates and 35 % vol. aromatic solvents) are needed for increase the octane number of gasoline while very small amounts (~100 ppm) are needed for the additives based on metals. Therefore these organic compounds are not additives and are the components of gasoline. Fuel oxygenates are organic substances (oxygenated hydrocarbons) containing at least one oxygen atom in the molecule. As oxygenates contain oxygen atoms in their molecules less oxygen from the air is needed for the burning of gasoline. Oxygenates are alcohols and ethers soluble in gasoline. Their properties, benefits and disadvantages are described. Oxygenates are polar substances and solubility of water is significantly higher in oxygenates than in petroleum products (nonpolar hydrocarbons). The danger of water absorption and dissolution in blends gasoline/oxygenates and further separation of oxygenates from gasoline is analysed.

Anti-knock fuel additives based on metals (Pb, Mn and Fe) for increase the octane number of gasoline have disadvantages (in addition to toxicity of lead). These ‘metal’ additives are not fully burned, ash is formed and accumulated in engines and in catalytic converters as deposits, or emitted into the atmosphere. Nowadays organic compounds (*oxygenates* and aromatic solvents) are used for increase the octane number of gasoline and its better burning. Their advantage is that they are fully burned and ash is not formed. The disadvantage of these organic compounds is that large quantities (to 15 % vol. oxygenates and 35 % vol. aromatic solvents) are needed for increase the octane number of gasoline while very small amounts (~100 ppm) are needed for the additives based on metals. Therefore these organic compounds are not additives and are the components of gasoline. Aromatic solvents are benzene, toluenes, ethyl benzene, and xylenes (BTEX). Their use is restricted because of negative influence on emission of pollutants. Benzene is toxic, and thus

Table 3.1 Oxygenates adding to gasoline

Chemical type	Name	Short name	Formula	Maximum ^a % vol.
Ether	Methyl Tertiary-Butyl Ether	MTBE	$(\text{CH}_3)_3\text{C}-\text{O}-\text{CH}_3$	15
	Ethyl Tertiary-Butyl Ether	ETBE	$(\text{CH}_3)_3\text{C}-\text{O}-\text{C}_2\text{H}_5$	15
	Tertiary-Amyl Methyl Ether	TAME	$\text{C}_2\text{H}_5\text{C}(\text{CH}_3)_2-\text{O}-\text{CH}_3$	15
	Tertiary-Hexyl Methyl Ether	THEME	$\text{C}_3\text{H}_7\text{C}(\text{CH}_3)_2-\text{O}-\text{CH}_3$	15
	Tertiary-Amyl Ethyl Ether	TAEЕ	$\text{C}_2\text{H}_5\text{C}(\text{CH}_3)_2-\text{O}-\text{C}_2\text{H}_5$	15
	Diisopropyl ether	DIPE	$(\text{CH}_3)_2\text{CH}-\text{O}-\text{CH}(\text{CH}_3)_2$	10
Alcohol	Tertiary Octyl Methyl Ether	TOME	$\text{C}_5\text{H}_{11}\text{C}(\text{CH}_3)_2-\text{O}-\text{CH}_3$	15
	Methanol	MeOH	CH_3OH	3
	Ethanol	EtOH	$\text{C}_2\text{H}_5\text{OH}$	5
	Iso-propyl alcohol	IPA ^b	$(\text{CH}_3)_2\text{CHOH}$	10
	<i>n</i> -propanol		$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	
	<i>n</i> -butanol	BuOH	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	
	<i>tert</i> -butanol	GTBA ^c	$(\text{CH}_3)_3\text{COH}$	7
	Iso-butyl alcohol	IBA ^d	$(\text{CH}_3)_2\text{CHCH}_2\text{OH}$	10
	sec-Butanol ^e		$\text{CH}_3\text{CHOHCH}_2\text{CH}_3$	

^a Maximum allowable values are defined by standard EN 228 [1]. Other oxygenates 10 % vol.

^b IPA Isopropanol

^c GTBA Gasoline grade *t*-butanol, named also Tertiary-Butyl Alcohol (TBA), or 2-methylpropan-2-ol (2-methyl-2-propanol)

^d IBA Isobutanol, or 2-methyl-1-propanol, or 2-methyl propyl alcohol

^e Secondary butyl alcohol 2-Butanol

is undesirable component of gasoline. The maximum allowable concentration of benzene is 1 % vol. and other aromatics is 35 % vol. in gasoline.

Other group of organic compounds is *fuel oxygenates*. They are organic substances (oxygenated hydrocarbons) containing at least one *oxygen atom* in the molecule. As oxygenates contain oxygen atoms in their molecules less oxygen from the air is needed for the burning of gasoline. Oxygenates are *alcohols* and *ethers* soluble in gasoline (Table 3.1). Fuel oxygenates were developed in the 1970s as octane enhancers to replace toxic TEL and are now accepted components of gasoline, sometimes named reformulated gasoline.

3.1 Alcohols as Fuel Oxygenates

Historically, oxygenate ethyl alcohol (ethanol $\text{C}_2\text{H}_5\text{OH}$) was used as a fuel in automobile internal combustion engine by the German inventor Nikolaus August Otto in 1876. The mixture 90 % vol. gasoline and 10 % vol. ethanol (named *gasohol*) is used in the USA.

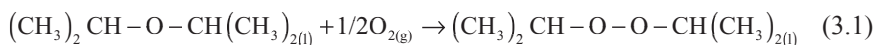
Methyl alcohol (methanol CH_3OH) is the cheapest of the oxygenates in part because of discoveries of natural gas in many places around the world. Natural gas (the principal constituent is methane CH_4) is the source for producing methanol. Methanol per se cannot be blended with gasoline because of compatibility prob-

lems with gasoline, particularly in the presence of water. In order to make methanol useful in gasoline, it must be combined with co-solvent alcohols (ethanol, propanols, and butanols). Methanol–gasoline blends M5 (5% vol. methanol in gasoline) with co-solvent alcohols were introduced in Europe and the USA in 1980s. Propanol (propyl alcohol) has two isomers and butanol (butyl alcohol) has four isomers, therefore usually mixtures propanols and butanols are used. These co-solvent alcohols prevent the separation of methanol from the gasoline that can take place in the presence of water. Propanols and butanols are also effective octane improvers but did not find wide application.

3.2 Ethers as Fuel Oxygenates

Methanol is the source for the producing another oxygenate methyl tertiary-butyl ether (MTBE). The manufacture of MTBE grew intensively in 1980s. MTBE is the most cost effective of oxygenates because of its high octane number, low vapor pressure, and excellent compatibility with gasoline. Among ethers, MTBE is most spread but ETBE and TAME are also used.

During storage in the presence of air, some ethers can be slowly oxidized with formation of peroxides (Eq. 3.1). These peroxides can be unstable and hazardous. Moreover, they can reduce octane number of gasoline. Ethers with alpha hydrogen atoms attached to the carbon adjacent to the ether linkage, such as diisopropyl ether (DIPE), are most susceptible to oxidation (Eq. 3.1):



Ethers MTBE, ETBE and TAME, with no labile methylene hydrogen atoms will be least prone to undergo this oxidation under normal storage conditions. Therefore peroxide formation in gasolines containing these three ethers should not be a problem especially since antioxidants are added to prevent oxidation of olefins also present in the fuel.

Unlike some ethers, alcohols are not known to oxidize under normal storage conditions.

Two important problems of oxygenates's use exist: solubility in water and materials compatibility. Oxygenates usually are not corrosive to metals (excluding methanol and ethanol, see Sect. 5.5.1) but are aggressive to some polymers and organic coatings (see Sect. 6). We will discuss how water dissolves in oxygenated fuels.

Oxygenates (alcohols and ethers) are polar substances and solubility of water (also polar substance) is significantly higher in oxygenates than in petroleum products (nonpolar hydrocarbons). Alcohols and ethers behave differently regarding water dissolution. Alcohols are more polar than ethers therefore water is more soluble in alcohols than in ethers. If water is fully dissolved in methanol and ethanol, water is partly dissolved in MTBE at 20 °C. Therefore, gasoline/ethanol blends can dissolve much more water than conventional gasoline, whereas gasoline/MTBE blends

act nearly like conventional gasoline in the presence of water. When the water reaches the maximum amount that the gasoline blend can dissolve, any additional water will separate from the gasoline. The amount of water required for this phase separation to take place varies with content of aromatics and alcohol in gasoline and temperature. For instance, water can be absorbed by a blend of 90% gasoline and 10% ethanol up to a content of 0.5% vol. at $\sim 15^{\circ}\text{C}$ before it will phase separate. This means that one teaspoon (~ 3 g) of water can be dissolved per 1 l of the fuel before the water will begin to phase separate. The gasoline/methanol blends are even more sensitive to water: water can be absorbed by a blend of 85% gasoline and 15% methanol up to a content of 0.1% vol. at $\sim 15^{\circ}\text{C}$ before it will phase separate.

Since MTBE has much less affinity for water than does methanol and ethanol, phase separation for gasoline/MTBE blends occurs with 10 fold small amount of water. A blend of 85% gasoline and 15% MTBE can hold only 0.625 g water (5 times less than gasoline/ethanol blend) at $\sim 15^{\circ}\text{C}$ per 1 l of the blend before water will phase separate. Similar to MTBE, ETBE also reduces in part the problem of water mixing with the fuel as it allows up to 0.4% water presence without gasoline separation. For comparison, 1 l of pure gasoline can dissolve only 0.012 g water (250 times less than gasoline/ethanol blend and 52 times less than gasoline/MTBE blend). Since oxygenated gasoline can hold more water than conventional gasoline, phase separation is less likely to occur with oxygenates present. The phase separation of blends gasoline/alcohol in the presence of water occurs at lower concentrations of alcohols than ethers in the blends gasoline/ether in the presence of water. Therefore maximum allowable concentrations of methanol and ethanol in gasoline are 3 and 5% vol. correspondingly while that of ethers is 15% vol. (see Table 3.1). The phase separation of gasoline/alcohol blends in the presence of water can cause corrosion of tanks (see Sect. 5.5).

Relatively high affinity of MTBE for water (in comparison with gasoline) was the cause of MTBE contaminants in ground water and banning of use of MTBE in gasoline in some states in the USA. If water appears in storage tank containing blend gasoline and MTBE, the latter will be extracted into water from gasoline. The solubility of gasoline containing 10% wt. MTBE in water is about 5,000 ppm whereas that of non-oxygenated gasoline is about 120 ppm at ambient temperature. When MTBE is in the soil as a result of a gasoline blend release, it may separate from the rest of gasoline, reaching the ground water first and dissolving rapidly. Once in the ground water, MTBE travels at about the same rate as the ground water whereas aromatics and other gasoline constituents tend to biodegrade and adsorb to soil particles. Thus MTBE affects ground water quality. In California (USA) there were a large number of private wells which used the ground water as potable water. Taste and odor thresholds for MTBE are very low and can be detected at ~ 30 ppb in water. Gasoline/MTBE blend spills to the land surface and releases from above-ground and underground storage tanks were the sources of contamination by MTBE. The MTBE contaminant tainted the water.

To sum up, fuel oxygenates and aromatic solvents help to keep clean air by replacing TEL, but they also have problems. Benzene is toxic. The presence of MTBE

in water gives strong odor and taste. Alcohols have to be blended with the gasoline at the distribution terminal, not at the refinery, because they tends to separate.

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Chapter 4

Biofuels

There is fuel in every bit of vegetable matter that can be fermented.

Henry Ford (1863–1947), an American industrialist.

Abstract People used some petroleum products from ancient times. Intensive use of crude oil started only in the twentieth century. The Russian chemist Mendeleev said that the burning of crude oil and fuels producing from it is the same as to throw the banknotes into the furnace. Numerous chemicals are producing from crude oil, namely, polymers, solvents, and medicines. In any case, the huge amount of crude oil is spent on producing of fuels. Nobody knows exactly how many stocks of crude oil are inside the earth crust and how many years we will be able to distill it and produce fuels. Crude oil is an exhaustible source for producing fuels. The first oil crisis in 1973 and the second one in 1991 caused many countries to search for alternative or renewable fuels. Alternative fuel is any fuel that is substantially non-petroleum and yields energy security and environmental benefits (air quality). Alternative fuels include biofuels, coal-derived liquid fuels, hydrogen, compressed natural gas, liquefied natural gas, liquefied petroleum gas, and dimethyl ether. **Biofuel** is a general name of fuels derived from renewable sources, sometimes called biomass. Liquid biofuels are subdivided on bioalcohols and biodiesel. They can be used as separate fuels or as components in conventional fuels (blends): bioalcohols in gasoline and biodiesel in diesel fuel. The properties of bioalcohols (mostly methanol and ethanol) and biodiesel, benefits, drawbacks, and additives are analysed.

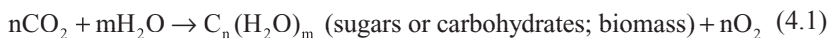
People used some petroleum products (bitumen and some other fractions of distilled crude oil) from ancient times (see Sect. 10). Intensive use of crude oil started only in the twentieth century owing to the development of numerous vehicles and industry. The Russian chemist Dmitri Ivanovich Mendeleev (1834–1907) once said that the burning of crude oil and fuels producing from it is the same as to throw the banknotes into the furnace. Really, nowadays numerous chemicals are producing from crude oil, namely, polymers, solvents, and medicines. In any case, the huge amount of crude oil is spent on producing of fuels. Nobody knows exactly how many stocks of crude oil are inside the earth crust and how many years we will be able to distill it and produce fuels. It is interesting to point out that development of fuels in our society depends on politics. The first automobile engines by Nikolas

August Otto and Henry Ford used ethanol. When the American Petroleum Institute was established in 1919, they began to promote the interests of the petroleum industry and thus protruded against use of ethanol in automobile engines. During the World War II Germany began producing synthetic fuel (named Ersatz) using Fischer-Tropsch process to help solve Germany's need for fuel in the midst of a crude oil shortage by converting coal, which was abundant in Germany. The Fischer-Tropsch process was invented in the 1920s by the German scientists Franz Fischer and Hans Tropsch. Another example is use of Fischer-Tropsch process of converting coal into gasoline in South Africa during apartheid regime in 1970s and international sanctions on crude oil import in this country.

Crude oil is an exhaustible source for producing fuels. It is not a renewable resource, meaning the supply is not endless. The first oil crisis in 1973 and the second one in 1991 caused many countries to search for *alternative* or *renewable fuels*. They also are called *non-conventional*, *non-traditional* or *advanced fuels*. *Alternative fuel* is any fuel that is substantially non-petroleum and yields energy security and environmental benefits (air quality). *Alternative fuels* include *biofuels* (*bio-based fuels*), coal-derived liquid fuels (Fischer-Tropsch process), hydrogen, compressed natural gas (CNG), liquefied natural gas (LNG), liquefied petroleum gas (LPG), and dimethyl ether (DME). We will describe only biofuels in this book.

Biofuel (abbreviation of *biorganic fuel*, sometimes called agrofuel) is a general name of fuels derived from renewable sources, sometimes called *biomass*. *Biomass* is biological material (plant and animal) from living or recently living matter, such as wood, other numerous types of plants, grass, algae (microorganisms) and organic wastes (manure, etc.). Biomass is generated by plant life. Chlorophyll in plants and sea-dwelling phytoplankton takes carbon dioxide (CO₂) out of the air and combine this with water using the energy they captured from sunlight to make sugars (carbohydrates) according to (4.1).

Sunlight energy



The process (4.1) is called photosynthesis. Biomass is organic material which contains carbon, hydrogen, and oxygen atoms (we need them in fuels!) and has stored sunlight in the form of chemical bonds which can be transformed in energy. Thus, biomass can be produced year after year on cropland. Therefore biomass is renewable. Like animal wastes. Strictly speaking crude oil was formed also from biological material which lived many billions of years ago. However, crude oil and fuels produced from it are named *fossil fuels*. Much more time (many billions of years) is needed to transform biomass to crude oil. Biomass using for production of biofuels can be grown or produced for several months.

Often liquid *biofuels* are subdivided on *bioalcohol* and *biodiesel*. They can be used as separate fuels or as components in conventional fuels (blends): *bioalcohol* in gasoline and *biodiesel* in diesel fuel. *Conventional (traditional) fuels* include fossil fuels (petroleum products from crude oil, coal, combustible slates, shale, wood, peat, natural gas) and nuclear materials, such as uranium or plutonium. We

Table 4.1 Alcohols using as fuels or their components in fuels

Name	Chemical formula	Boiling point, °C	Freezing point, °C	Density at 20 °C
Methanol (wood alcohol, methyl alcohol)	CH_3OH	65	−96	0.791
Ethanol (grain alcohol, ethyl alcohol)	$\text{C}_2\text{H}_5\text{OH}$	78	−116	0.793
Propanol (n-propanol; propan-1-ol)	$\text{C}_3\text{H}_7\text{OH}$ ($\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$)	97.2	−126	0.803
Isopropanol (isopropyl alcohol; propan-2-ol)	$\text{C}_3\text{H}_7\text{OH}$ ($\text{CH}_3\text{CHOHCH}_3$)	82.4	−86	0.786
Butanol (n-butanol, n-butyl alcohol, butanol-1)	$\text{C}_4\text{H}_9\text{OH}$ ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$)	117.25	−89	0.811
Butanol-2 (isobutanol)	$\text{C}_4\text{H}_9\text{OH}$ ($\text{CH}_3\text{CHOHCH}_2\text{CH}_3$)	99.5	−114.7	0.8063
2-methyl-propanol-2 (isobutanol)	$\text{C}_4\text{H}_9\text{OH}$ ($\text{CH}_3\text{C}(\text{CH}_3)\text{OHCH}_3$)	82.2	25.5	0.7887
2-methyl-propanol-1 (isobutanol)	$\text{C}_4\text{H}_9\text{OH}$ ($\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{OH}$)	108.4	−108	0.8027

will describe only liquid *biofuels* and then how they influence metals, alloys, and polymeric materials (see Sects. 5.5 and 6.3). Use of biofuels has some benefits, such as attenuation the dependency on fossil fuels, improvement air quality and reduction in greenhouse gas emissions, easy available and renewable raw materials. However, biofuels have some disadvantages, mainly their compatibility with materials which are widely used in contact with conventional fuels.

Bioalcohols Four alcohols are used as biofuels: methanol, ethanol, propanols, and butanols (Table 4.1).

These alcohols are the same alcohols which are used as fuel oxygenates (see Sect. 3). Sometimes they are named *bioalcohols*, or *fuel grade alcohols* (FGA), or *synthetic fuel grade alcohols* (SFGA). Chemically they are the same molecules of alcohols but can differ by the presence of different contaminants. Ethanol which is used in beverages and medical application does not contain contaminants.

An alcohol is an organic compound in which the hydroxyl functional group (−OH) is bound to a carbon atom of the radical ($\text{C}_n\text{H}_{2n+1}$). Most common *fuel grade alcohol* is *ethanol* and less common are *methanol*, *propanols* and *butanols*. *Biobutanol* (also called *biogasoline*) is often claimed to provide a direct replacement for gasoline, because it can be used directly in gasoline engine. Bioalcohol contents are expressed as a percentage (volume) of bio-component in conventional fuel. For example, M15 is 15% vol. methanol in gasoline; E85 is 85% vol. ethanol in gasoline.

Methanol can be used alone or in combination with gasoline. Methanol can be produced from natural gas (the principal constituent is methane CH_4), coal (carbon C), and biomass. The first oil crisis in 1973 caused to begin using methanol in blends with gasoline as a liquid fuel. Thus methanol blends containing up to 15%

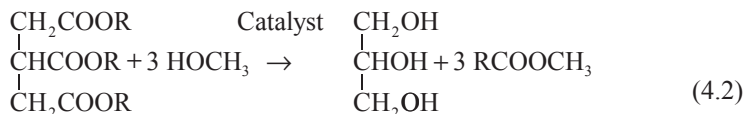
vol. (M15) were used in the later 1970s and the 1980s in Sweden, Germany, New Zealand, and China. Methanol can be used from several percents in gasoline (M3) up to neat methanol M100. Nowadays typically two fuels are used: M15 and M85.

Ethanol may be produced biochemically or by chemical synthesis (without use of biological objects). People used the first process from the ancient times as early as 9,000 years ago. Ethanol can be produced from any biological feedstock that contains glucose such as starch or cellulose. Glucose is fermented into liquid ethanol. *Ethanol* is the **only** alcohol used in beverages. ***Other alcohols are very poisonous. For instance, if a person will drink 10 ml of pure methanol it will cause blindness, and 30–100 ml will cause death.***

Ethanol may be used as a motor fuel in several ways: E10 (named gasohol in the USA), E15, E85, E95, and neat ethanol (E100).

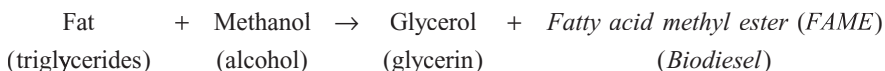
Denatured alcohol also is used as a fuel for spirit burners and camping stoves. *Denatured alcohol* is ethanol that has additives to make it more poisonous or undrinkable. These additives are called *denaturants*.

Biodiesel *Biodiesel* is a biofuel suitable for use in compression ignition (diesel) engines. It is composed of long-chain *fatty acid monoalkyl esters* (FAME— RCOOCH_3 or FAEE— RCOOC_2H_5) derived from plant oils, animal fats, microalgae, and recycled greases and oils. Biodiesel is produced through chemical process called transesterification:



or described by words:

Catalyst (NaOH or KOH)



Liquid product of the reaction (4.2), *fatty acid methyl ester (FAME)*, named also *esterified oil*, is *biodiesel*. If ethanol is used instead methanol, *fatty acid ethyl ester (FAEE)* is obtained. By-product of the reaction (4.2), glycerin, is used in cosmetics, urethane polymers, etc. Biodiesel can be made from methyl, ethyl, isopropyl, and other alcohols, but mostly the former is used. If soya oil is used for production of biodiesel, the latter has name *methyl soyate*; if rapeseed oil (canola or field mustard)—*Rapeseed Methyl Ester* (RME); when tallow fat—*Methyl Tallowate*. Esters are widespread in nature. Esters have remarkable application in everyday life. Owing to different flavor esters (chemically they are similar to FAME) we feel the

pleasant aroma of fruits. Each ester has its proper characteristic smell. Plexiglas and Dacron (fabric, polyesters) are polymeric materials based on esters.

The high molecular organic acids containing 16 and 18 carbon atoms (oleic, linoleic and palmitic acids) can be present in biodiesel. The higher saturated fatty acid content would cause higher oxidative and thermal stability. *Biodiesel* is similar in properties to conventional diesel fuel producing by distillation of crude oil.

The boiling point of biodiesel generally ranges from 330 to 357°C and of conventional diesel fuel from 180 to 370°C at 1 atm. In contrast to diesel fuel, biodiesel contains no sulphur. Emissions of CO, CO₂, non-burned hydrocarbons and particulates are reduced after combustion of biodiesel comparing with conventional diesel fuel. Emission of NO_x is increased but can be reduced by use of a catalytic converter. Rudolph Diesel was the first who used peanut oil as fuel for his engine in 1900 year. Blends of biodiesel with conventional diesel fuel are designated as 'B' followed by a number indicating the percentage (vol.) biodiesel. For example, B100 is pure biodiesel; B20 is 20% vol. biodiesel and 80% vol. conventional diesel fuel. Biodiesel can be used neat (B100), but is often blended with conventional diesel fuel (B20). Biodiesel can be used in several ways.

1. One to two % vol. biodiesel as a lubricity additive, which can be especially important for ultra low sulphur diesel fuels (ULSD, less than 10 ppm sulphur), which may have poor lubricating properties (see Sect. 2).
2. Blends (B20) for utilizing in most applications that use diesel fuel. In this case, a biodiesel is a component of the fuel.
3. Pure biodiesel (B100) as a fuel or as a solvent.

Conventional diesel fuel is allowed contain up to 7% vol. FAME according to the standard EN 590. Biodiesel is used both as automotive diesel fuel and as heating fuel. Biodiesel is used as a diesel additive to reduce concentrations of particulates, non-burned hydrocarbons and carbon monoxide from diesel vehicles and is most common *biofuel* in Europe.

Aboveground biofuel storage tanks should be protected with insulation, heating systems, and agitation. The most problems with biodiesel occur because of its high solvency (ability to dissolve another substances), tendency to absorb water and to swell some polymeric materials (see Sect. 6.3). The most common encountered problem with solvency is biodiesel's tendency 'to clean out' the inner surface of storage tanks, pipes and other systems. Usually conventional diesel fuel tends to form sediments that stick to and accumulate in storage tanks, forming layers of sludge or slime in the fuel systems. The older the system, and the poorer the maintenance, the thicker the accumulated sediments become. Biodiesel can dissolve these sediments and carry the dissolved solids into the fuel systems of vehicles. This means that first-time users of pure biodiesel will have to change their fuel filters more often than usually, unless they have had their fuel system cleaned prior to switching to biodiesel. Another problem of biodiesel use is the tendency to absorb water and as a result microbial contamination and corrosion (see Sects. 5.4 and 5.5.2).

4.1 Additives to Biofuels

Additives to methanol-gasoline blends Antioxidants, corrosion inhibitors, detergents, and co-solvents are added to methanol-gasoline blends.

4.1.1 Additives to Biodiesel

Cold flow additives (pour point depressants) are flow improvers of biodiesel in cold weather. Biodiesel can solidify at a higher temperature in cold weather than conventional diesel fuels, and usually the additives for conventional diesel fuels are less efficient with biodiesel. Most additives reduce the size of crystals or prevent crystal formation. Cold flow additives contain low molecular weight co-polymers of ethylene, vinyl acetate, and other olefin-ester co-polymers. The efficiency of these additives depends on the type (origin) of biodiesel and its content in blend. For instance, commercial cold flow additives are more effective in FAEE than in FAME. Cold flow additives are more efficient with biodiesel blends than with neat biodiesel.

Lubricity Blending biodiesel into conventional diesel fuel at even low concentrations can increase the lubricity of diesel fuel. As little as 0.25 % vol. biodiesel can significantly increase fuel lubricity. Some fleets use B2 for its lubricity properties instead of using other additives.

Metal chelating additives Certain metals (copper, zinc, tin, and lead) and alloys (brass and bronze) accelerate the degradation of biodiesel and form even higher amounts of sediments than would be formed in conventional diesel fuels. B100 should not be stored for long periods in systems that contain above mentioned metals and alloys. Metal chelating additives, which serve to de-activate these metals, may reduce or eliminate their negative impact.

Antistatic additives Pure biodiesel and its blends ($\geq 20\%$ vol. biodiesel in conventional diesel fuel) have sufficiently high electrical conductivity and a static dissipater is typically not required. However, small concentrations of biodiesel in blends ($< 20\%$ vol.) require the injection of antistatic additives.

Antioxidants Bleaching, deodorizing, or distilling oils and fats, either before or as a part of the biodiesel producing, can remove natural antioxidants from the finished biodiesel. Vegetable oils and fats are produced with natural antioxidants, such as polyphenolic compounds, ascorbic acid (Vitamin C), tocopherols (Vitamin E), and carotenoids—nature's way of protecting the oil from degradation over time. Tocopherols delay the oxidation of FAME by more than 10 times compared with FAME without tocopherols. The stabilizing effect of tocopherols depends on the origin of FAME. Oxidation of unsaturated fatty compounds in biodiesel begins with the build-up of peroxides. Irreversible oxidation, indicated by viscosity increase, starts only after a certain amount of the peroxides is reached. Tocopherols stabilize

the unsaturated organic compounds in biodiesel by reducing the rate of peroxide formation, thereby extending the time required to reach the peroxide concentration at which viscosity starts to increase. Synthetic and natural antioxidants' additives can significantly increase the storage life and stability of biodiesel. Synthetic antioxidants are more effective than natural ones. Keeping the biodiesel without contact with air reduces or eliminates biodiesel oxidation and increase storage life. This can be done using a nitrogen blanket on fuel tanks or storing biodiesel in sealed drums or totes for smaller amounts of biodiesel. If the fuel turn over is in a range of 2–4 months, the biodiesel stability is not a problem. It is recommended to store the B100 not more than 6 months, otherwise antioxidants should be added. In spite of B20 can be stored for 8–12 months it is recommended that B20 be used within a half of a year. Adding antioxidants and/or stability additives is recommended for storage over longer periods.

The grains (e.g., corn) and sugar crops (e.g., sugar cane, beets, etc.) for bioalcohol and oil seed crops (e.g., rape, soy, etc.) for biodiesel constitute the first generation biofuel sources. The agricultural residues (e.g., corn stover) and grasses (e.g., miscanthus) for bioalcohol and high-oil vegetables (e.g., jatropha) for biodiesel constitute the second generation biofuel sources. Cellulosic materials for bioalcohol and algae or other non-food biomass (microorganisms and plants) for biodiesel form the third generation biofuel sources. Integrated biorefining complexes are developing in 2010–2020s. Each succeeding generation of biofuel source is considered to be more sustainable.

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Chapter 5

Corrosion of Metallic Constructions and Equipment in Petroleum Products

*From Big Bang to Bigger Boom
One thing just we may assume:
Universe-roulette-wheel spins
Order loses! Chaos wins!*

Wystan Hugh Auden (1907–1973), Anglo-American poet

Abstract General theory of corrosion, corrosion mechanisms and phenomena that take place with metals contacting petroleum products are described: differential aeration cell, uniform and different types of localized corrosion (pitting, crevice, and galvanic corrosion). Corrosion mechanism with participation of water and dissolved oxygen in petroleum products is suggested. The corrosion process proceeds at the interface between the two phases, metal/fuel—water (similar to the interface metal/air-water). Electrical conductivity of petroleum products, its physico-chemical character, experimental data and relationship to corrosiveness is described and explained.

Microbial contamination of fuels and biodiesel, its consequences and prevention are described and analysed. Participation of microorganisms in corrosion of metals in fuels, mechanism, examples and preventive measures are given. Corrosion in biofuels (alcohols and biodiesel), mechanism, stress corrosion cracking of carbon steel in methanol and ethanol, preventive measures, material compatibility with alcohols and biodiesel are described in detail. As many tanks and pipelines are used in the atmosphere and soil, corrosion, its causes, prevention and control in these two environments also are described. Special attention is given to corrosion of aboveground storage tanks (AST), its types, and corrosion zones. Experimental study of corrosion of inner surfaces of 35 AST (10 gasoline, 4 kerosene, 6 gas oil, 14 fuel oil, and one crude oil) is described. Corrosion rates of carbon steel shells, roofs and bottoms of AST after 55–70 years of service are documented and analysed. Corrosion of tanks and pipelines under thermal insulation and preventive measures are described.

Most metallic constructions and equipment which contact petroleum products are made of carbon steel and are exploited at ambient temperature which can range between -50°C and $+50^{\circ}\text{C}$ in different regions of our planet. When metals and alloys contact pure hydrocarbons (C_nH_m), they do not react with them. However,

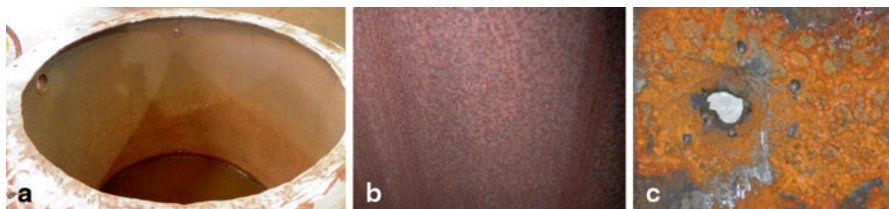


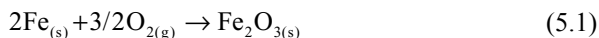
Fig. 5.1 **a** tank containing light naphtha, **b** inner surface of the shell of the aboveground storage tank (AST) containing gasoline, **c** the bottom of the AST containing gas oil

we can observe rust in tanks and pipelines containing gasoline, naphtha, and gas oil (Fig. 5.1).

Rust is the product of corrosion of iron in water, in aqueous solutions of electrolytes, in humid atmosphere, and in soil. How can rust be formed in tanks and pipelines containing petroleum products? Which constituents in petroleum products can cause corrosion of metals and alloys? What is the corrosion mechanism in petroleum products? In order to reply these questions, we should be familiar with the general theory of corrosion.

5.1 General Theory of Corrosion

Our basic point is that *corrosion is the reaction between a metal and the environment*. There are two corrosion mechanisms: by non-electrolytes and in the presence of electrolytes. Non-electrolytes are the substances that do not dissociate into ions and do not conduct electric current being dissolved in water. Electrolytes are the substances whose water solutions conduct electric current on account of free ions (H^+ , Na^+ , Ca^{2+} , OH^- , Cl^- , SO_4^{2-} , etc.). Pure water is weak electrolyte. Sea water is an aqueous solution of strong electrolytes (mostly $NaCl$ and $MgSO_4$). Non-electrolytes are gaseous oxygen (O_2) and liquid sulfur (S_8). When iron meets gaseous O_2 or liquid S_8 , it reacts according to reactions:



Thus, if carbon steel contacts hot atmosphere in the furnace or liquid sulfur in petroleum products, it can corrode according to reactions (5.1) and (5.2) respectively. These corrosion reactions occur under ‘dry’ conditions: without water, or more precisely, without electrolyte. Sometimes this mechanism is called ‘dry’ or ‘chemical’ corrosion because there is no electric current on metal contacting non-electrolytes.

The second corrosion mechanism in the presence of electrolytes is more spread because water is present in the atmosphere, in soil and also can be dissolved in fuels. When carbon steel construction is immersed in water containing dissolved oxygen,

the iron corrodes in anodic reaction (5.3) and liberated electrons are taken away by dissolved oxygen in cathodic reaction (5.4). Anodic, or oxidizing, process—passing of positive metallic ions into solution and releasing of electrons on the metal surface:



Cathodic, or reduction, process—any process of receiving of electrons:



If iron contacts acidic solution another cathodic process occurs:



Oxygen contained in an atmosphere in a quantity of ~21 %, dissolves in water. The solubility of oxygen in water is not great, about 0.0008 % wt. (8 ppm), but this amount is enough for corrosion to occur. Two electrochemical reactions, anodic (5.3) and cathodic (5.4 or 5.5), occur simultaneously. Elimination of one of these processes will decrease corrosion of a metal. Thus removing dissolved oxygen from water we can significantly decrease corrosion. This corrosion mechanism in the presence of electrolytes is called electrochemical corrosion.

Usually metals encounter not pure water but aqueous solutions containing different salts. Therefore it is important to emphasize that corrosion rate of iron in such solutions depend on salt content. Corrosion rate will increase with increase of salt concentration in water according to the equation (5.6):

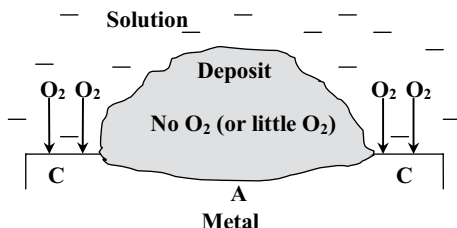
$$I_{\text{corr}} = E/R \quad (5.6)$$

I_{corr} —an electric current (corrosion rate); E —an electric potential difference between cathode and anode; R —an electrical resistance of an electrolyte. When salt (or any other electrolyte) is added to water, electrical resistance of the electrolyte solution (R) diminishes, and corrosion current I_{corr} (corrosion rate) increases according to (5.6). That is why corrosion of carbon steel equipment in sea water is larger than that in tap or river water.

When metallic equipment contacts water, soil or atmosphere of high humidity, electrochemical corrosion occurs with the participation of water and dissolved oxygen. The result is a brick-reddish-brown rust $\text{FeO} \cdot \text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ which is not dissolved in water (see Fig. 5.1).

Differential aeration cell We often observed the uneven spreading of rust inside and outside of tanks and pipelines containing fuels, sometimes shallow pits under deposits on carbon steel surface in fuels, soil or in water, and severe corrosion of various structures and equipment on the interface water-fuel, air-soil, or air-water. If two sites on a carbon steel surface differ in dissolved oxygen concentrations, these sites acquire different electric potentials, and a *differential aeration cell* appears (Fig. 5.2). A carbon steel surface with a larger dissolved oxygen concentration on it will be a cathode (oxygen participates in reduction process), and will not

Fig. 5.2 Differential aeration cell forms in the presence of any deposits. *C* cathode, *A* anode



corrode. A carbon steel surface with a smaller dissolved oxygen concentration on it will be an anode (electric potential will be less than that of the site with a high oxygen concentration), and will corrode.

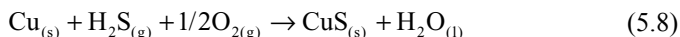
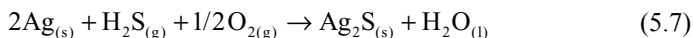
Differential aeration cells are responsible for the pitting corrosion, crevice corrosion, corrosion of structures and equipment at the interface air–water, air–soil, corrosion in fuels, and corrosion in soils.

Diverse corrosion phenomena exist. We will describe them in the next section.

5.2 Corrosion Phenomena

There are both many metals (about 80 and significantly more alloys—thousands!) and a lot of environmental types (of course, more than 80!), and we might expect many different corrosion phenomena. In spite of this, all corrosion phenomena are divided into two types: uniform (general) and non-uniform (localized) corrosion (Fig. 5.3).

Uniform corrosion is a process when all of a metal surface corrodes evenly. When we put copper or silver strip in jet fuel in order to examine presence of hydrogen sulphide or other sulphur-containing compounds, and the surface of these metals blackens, general corrosion occurs:



Localized corrosion is a process when only some definite parts of a metal surface corrode. This corrosion type is more spread than a uniform corrosion. Localized corrosion can occur in fuel systems (containing water and electrolytes) as pitting, crevice, galvanic, microbiologically induced corrosion (MIC), stress corrosion cracking (SCC), erosion, and cavitation. They result in two main forms: pits and cracks.

Pitting Corrosion Pits may appear as a result of presence of chloride (Cl^-) anions in the environment, the existence of differential aeration cells, crevice corrosion, galvanic corrosion, MIC, erosion, and cavitation. First we shall explain how chlorides cause pitting corrosion.

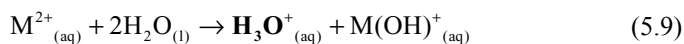
Stainless steel has passive film Cr_2O_3 , iron and carbon steels—mixed oxides (FeO , Fe_3O_4 , and Fe_2O_3), aluminum— Al_2O_3 . These passive films are prone to be



Fig. 5.3 **a** Uniform (general) corrosion of carbon steel, **b** pitting corrosion of carbon steel, **c** stress corrosion cracking of stainless steel 316

attacked by chloride anions because of defects of such films and because of heterogeneity of surface under the films. Defects in the film may be pores, cracks, any imperfections, inclusions (chemical compounds).

Chloride anions may penetrate through these films and destroy them because of more positive electric potentials at some heterogeneous inclusions (for example, manganese sulphide), than pure alloy. If chlorides penetrate through passive film, they can attract iron or chromium cations from the alloy lattice. This process is provided by hydrolysis with the formation of acidic medium in the localized point:



M^{2+} means Cr^{2+} or Fe^{2+} . Ions H_3O^{+} and Cl^{-} make for presence hydrochloric acid in the solution and result in low pH (even less than 1!) at the imperfections of the passive film. This acid is formed in pits on stainless steel surface. The solution around these pits is neutral. Because of the heterogeneity of stainless steel surface under passive film, pits of various shape, density and size are formed. Depending on nature of metals and alloys different low pH values may be received in pits on metallic surface. Not only chlorides ions can cause pitting corrosion. Any inorganic and organic deposits can result in formation of differential aeration cells and then to pitting corrosion underneath.

Crevice Corrosion This is localized corrosion of a metal surface at an area that is shielded from full exposure to the liquid electrolyte because of close proximity between the metal and the surface of another material (metallic or non-metallic) and stagnant conditions of the liquid in this area (Fig. 5.4). Crevice means narrow crack or opening, a fissure or cleft. Existence of differential aeration cell can explain this phenomenon. Let us imagine the gap (narrow space, crack, groove or slot) between two surfaces (metal-to-metal or metal-to-non-metal), wide enough to permit liquid electrolyte entry, but sufficiently narrow to maintain a stagnant zone. Dissolved oxygen in liquid electrolyte inside the gap (crevice) will be used up in cathodic reaction (5.4) and its concentration will decrease to zero, as oxygen diffusion into the crevice is restricted. Opposite, the concentration of dissolved oxygen in bulk electrolyte solution near the crevice will remain the same (~ 8 ppm in neutral aqueous solutions at $\sim 20^{\circ}C$). Thus, *differential aeration cell* (oxygen concentration cell) is formed. The metallic surface in bulk solution near the crevice

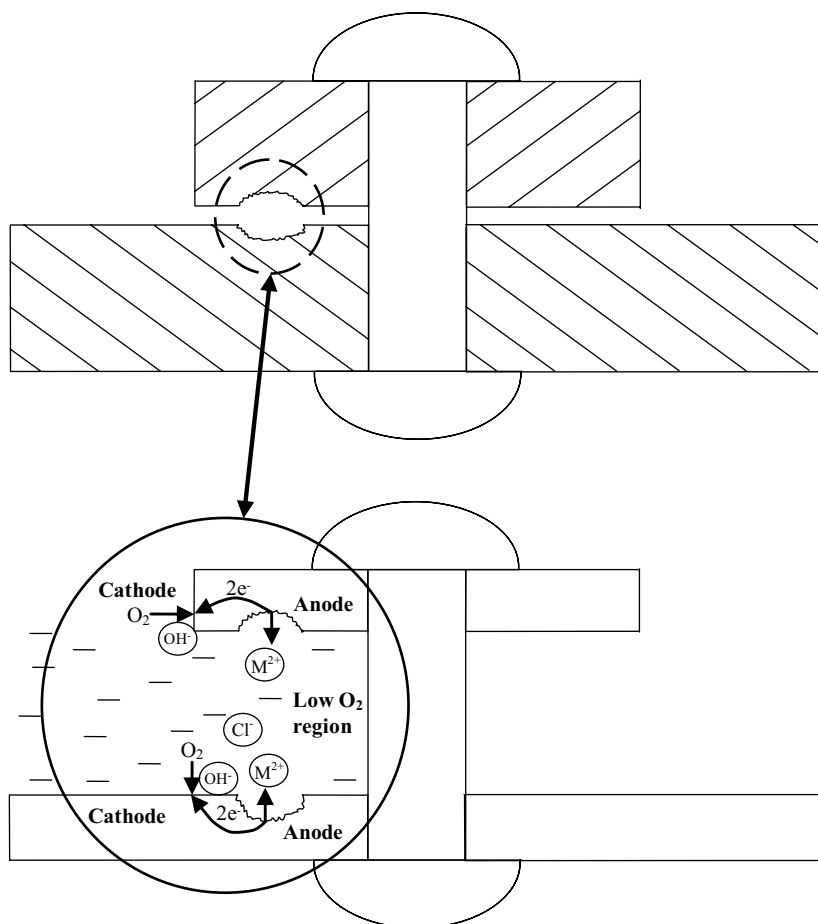


Fig. 5.4 Crevice corrosion mechanism

will be cathodic (high oxygen concentration) and the surface inside crevice will be anodic (low, nearly zero, oxygen concentration) with appropriate electrochemical reactions (5.4) and (5.3). As a result, deep pits may be formed at a carbon steel surface over several months (Fig. 5.5). Therefore, crevice corrosion sometimes is considered as a particular form of pitting corrosion which occurs between faying surfaces.

Crevice corrosion is initiated by changes in local chemistry within the crevice: decrease of oxygen concentration, decrease pH, decrease inhibitor concentration, or increase of Cl^- content. Therefore, not always crevice corrosion occurs due to differential aeration cell. This explains why crevice corrosion is also observed on alloys like stainless steels in chloride solutions where oxygen is absent, and no oxygen concentration cell exists.

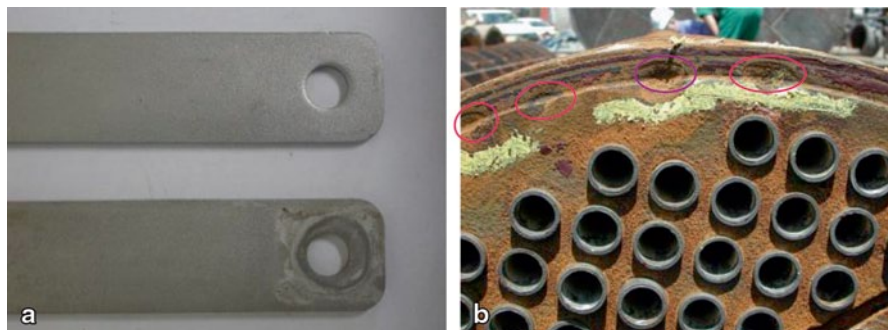


Fig. 5.5 **a** Crevice corrosion between a metal and non-metal: *the upper*—original carbon steel coupon, *the lower*—carbon steel coupon after the contact with polypropylene washer in water during 120 days. **b** Crevice corrosion between a metal and metal (tubesheet and gasket made from carbon steel in heat exchanger, cooling water, 4 years)

Crevices may be of two types: man-made artificial and natural. The former may be unavoidable and may serve a particular design purpose of construction, such as fasteners, gaskets, lap joints, rivets, etc. Other man-made crevices may result during fabrication and assembly. Some of them may be avoidable. Different coatings, sealants and greases can promote crevice corrosion. Natural crevices may be formed by any deposits: debris, rust, scale, sediments, barnacles, mussels, and biofouling.

The methods of minimizing or prevention crevice corrosion:

- a. Elimination crevices at the design and fabrication stages, and then during service. For example, design tanks, vessels, pumps and other equipment for complete drainage; avoid stagnant areas and sharp corners.
- b. Use welded butt joints instead of bolted or riveted joints. Close crevices in lap joints by continuous welding, caulking, or soldering. Seal lap joints and avoid gaps between pipes and fittings. Minimize use of bolted connections and fasteners.
- c. Decrease dimensions of the gap: degree of tightness. Tighter crevices can be achieved between nonmetal and metal components than between two metals.
- d. Inspect equipment.
- e. Drain equipment completely on shutdowns. Remove deposits regularly.
- f. Prevent wetting polymeric materials, and remove wet packing materials periodically. Use nonabsorbent (non-porous) gaskets and seals (Teflon, etc.).

Galvanic Corrosion There is almost no equipment made of only one type of metal or alloy. Look at any tap, a pump, a pipeline, a truck and we will detect the parts made of dissimilar metals or alloys joining together. When such equipment is in a dry atmosphere or contacts non-electrolyte liquids (crude oil or any petroleum product possessing low electrical conductivity) nothing occurs. However, if the same equipment contacts electrolyte, corrosion of a metal with less electrode potential in the electromotive force series will occur (Table 5.1).

Table 5.1 Electromotive Force Series

Electrode reaction	Standard potential at 25 °C, Volts versus SHE
$\text{Ag}^+_{(\text{aq})} + \text{e}^- \leftrightarrow \text{Ag}_{(\text{s})}$	0.800
$\text{Cu}^{2+}_{(\text{aq})} + 2\text{e}^- \leftrightarrow \text{Cu}_{(\text{s})}$	0.337
$2\text{H}^+_{(\text{aq})} + 2\text{e}^- \leftrightarrow \text{H}_{2(\text{g})}$	(Reference 0.000)
$\text{Pb}^{2+}_{(\text{aq})} + 2\text{e}^- \leftrightarrow \text{Pb}_{(\text{s})}$	-0.126
$\text{Sn}^{2+}_{(\text{aq})} + 2\text{e}^- \leftrightarrow \text{Sn}_{(\text{s})}$	-0.136
$\text{Ni}^{2+}_{(\text{aq})} + 2\text{e}^- \leftrightarrow \text{Ni}_{(\text{s})}$	-0.250
$\text{Cd}^{2+}_{(\text{aq})} + 2\text{e}^- \leftrightarrow \text{Cd}_{(\text{s})}$	-0.403
$\text{Fe}^{2+}_{(\text{aq})} + 2\text{e}^- \leftrightarrow \text{Fe}_{(\text{s})}$	-0.440
$\text{Cr}^{2+}_{(\text{as})} + 2\text{e}^- \leftrightarrow \text{Cr}_{(\text{s})}$	-0.91
$\text{Zn}^{2+}_{(\text{as})} + 2\text{e}^- \leftrightarrow \text{Zn}_{(\text{s})}$	-0.763
$\text{Mn}^{2+}_{(\text{as})} + 2\text{e}^- \leftrightarrow \text{Mn}_{(\text{s})}$	-1.18
$\text{Al}^{3+}_{(\text{as})} + 3\text{e}^- \leftrightarrow \text{Al}_{(\text{s})}$	-1.66
$\text{Mg}^{2+}_{(\text{as})} + 2\text{e}^- \leftrightarrow \text{Mg}_{(\text{s})}$	-2.37

SHE Standard Hydrogen Electrode

Fig. 5.6 Galvanic corrosion of carbon steel baffles in contact with titanium tubes in cooling water, 4 years



The Table 5.1 is for some metals often using in construction and equipment (full tables for metals and alloys are shown in ([1], pp. 20, 65).

Galvanic corrosion is a corrosion phenomenon occurring when two different metals or alloys (or any conductor, for example, graphite) are in contact in general electrolyte (Fig. 5.6).

Metallurgical, environmental, electrochemical, and geometrical factors influence galvanic corrosion. Geometrical factors include the ratio between anode and cathode area, the distance between them, the geometrical forms of dissimilar met-

als, and type of joint between anode and cathode (welded, fasteners, or separate by external conductive connection).

The large variety and complexity of all these factors point out that it is difficult to predict the galvanic corrosion occurrence. This is very important to engineers who design new equipment, or upgrade old equipment. Three main factors define the correct choice of dissimilar metal contacts: the difference of electrode potentials of various metals in equipment, the ratio between anode and cathode areas, and the electrical conductivity of media. The more the difference of electrode potentials between metals, the more severe galvanic corrosion that will occur. The value of 250 mV is usually defined as a “non-dangerous” one, or galvanic corrosion with very low insignificant rate. The smaller the ratio of the anode to cathode area and the more the electrical conductance of a medium, the faster galvanic corrosion of the anode will occur. The methods of minimizing or prevention galvanic corrosion:

- a. Do not select dissimilar metals, alloys or other conductive materials (for example, graphite) that have a difference in electrode potentials of more than 250 mV between them.
- b. Select an anode more than a cathode area.
- c. Use insulators between dissimilar metals.
- d. Design a convenient way for the change of anode parts, and/or produce them thicker.

5.3 Corrosion in Petroleum Products

If rust was detected in tank or pipe containing fuels (see Fig. 5.1), this means that water and dissolved oxygen took part in corrosion of carbon steel structures according to electrochemical mechanism (see reactions 5.3 and 5.4). The water content in fuels produced at oil refineries is usually low (30–80 ppm) and is not sufficient to make them corrosive. If gasoline contacts carbon steel equipment in dry conditions, the equipment does not corrode. Water vapors may ingress from the atmosphere into fuels during their storage and transportation. Then water vapors may condense as a result of temperature decrease, and the water content in fuels may reach concentrations more than 80 ppm (see Sect. 1.2.1.1 and Appendix D). An increase of water content in fuels results in a drastic increase in the corrosion rate of carbon steel. For instance, the corrosion rate in “dry” gasoline (80 ppm or 0.008 % wt. dissolved water) is 0.001 mm/year, and when 200 ppm (0.02 % wt.) water is added, the corrosion rate is 0.4 mm/year (Fig. 5.7).

The concentration of water in fuel when corrosion rate increases drastically, we call the critical value. The value 200 ppm water in gasoline is critical. When 200 ppm of water is added to gasoline, all of this water is soluble (in the solution gasoline-water). These results suggest that the corrosion process in gasoline-water mixtures is caused by the soluble water in the gasoline (one phase). The critical

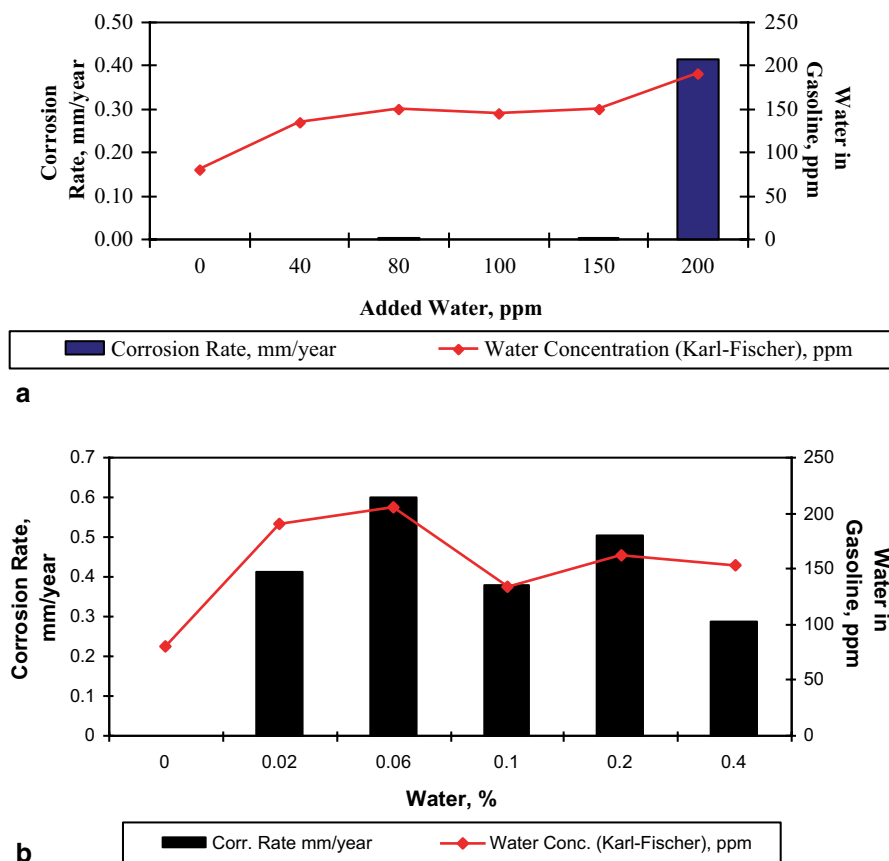


Fig. 5.7 Corrosion rate of mild steel and water content in gasoline vs. added water to gasoline [2]. Mild steel is low-carbon steel which contains up to 0.2% wt. carbon. Soluble water content in gasoline was determined by the Karl-Fischer method [3]

value of water content in naphtha and kerosene was defined as 1,000 ppm. The presence of aromatics and oxygenates in fuels and increase of temperature cause the rising of the solubility of water in fuels. When temperature decreases water can separate and appear as free water phase on metal surface.

Another “actor” participating in electrochemical corrosion, oxygen, is dissolved significantly better in hydrocarbons than in water (see Sect. 1.2.1.2 and Appendix E). The oxygen solubility in hydrocarbons (60–70 ppm) is higher than in the aqueous phase (8 ppm). This situation results in corrosion mechanism similar to atmospheric corrosion in thin layer of electrolyte (see Sect. 5.6). As atmosphere containing 21% vol. O_2 supplies thin water layer by oxygen (8 ppm), fuel (containing ~70 ppm O_2) also supplies water layer forming on carbon steel surface by oxygen needed for electrochemical corrosion to occur (Fig. 5.8). Another assumption is that the corrosion mechanism in the two-phase system petroleum

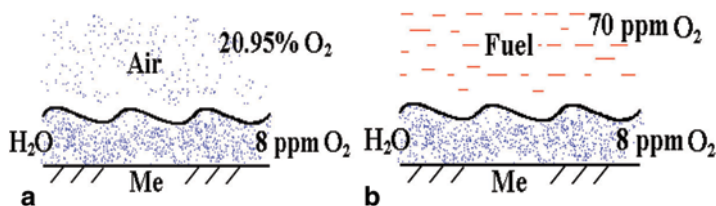


Fig. 5.8 Corrosion mechanism: **a** in atmosphere, **b** in fuel

product-electrolyte is similar to the corrosion at the splash zone above high tide. In both cases, the organic phase plays the role of the atmosphere that supplies water, oxygen, and other corrosives.

The corrosion process proceeds at the interface between the two phases, metal/fuel—water (similar to the interface metal/air-water). In a fuel-water environment, a metal is partially wetted by the water that creates a thin water layer between the metal and organic phase. The average thickness of the water layer is 2–10 μm . One can imagine this two-phase system being a differential aeration cell (see Sect. 5.1). These cells mostly are responsible for corrosion in water, in atmosphere, in soil, and in splash zone. An anodic area is formed in the water phase (low oxygen concentration, ~ 8 ppm) and a cathodic area (high oxygen concentration, ~ 70 ppm) in the fuel phase (Fig. 5.9).

Parameters that affect the corrosion process in the metal/fuel—water system are water concentration in the mixture, appearing of free water, electrical conductivity, type and concentrations of electrolytes in water, temperature, and fluid velocity. Different salts and organic acids present in the petroleum products can undergo extraction from the fuel into the aqueous phase and cause an increase in the corrosion rate of carbon steel (Table 5.2). These data show a drastic increase in water conductivity after contact with petroleum products. This means that petroleum products are the source of anions (Cl^- , SO_4^{2-} , and NO_3^-) and light organic acids (formic HCOOH and acetic CH_3COOH) and that they are probably responsible for the corrosiveness of the fuels in the presence of water. Decrease of water pH after contact with petroleum products also confirms the presence of acidic salts and organic acids. Organic acids can appear in fuels as a result of oxidation of hydrocarbons during their treatment or storage, as well as wastes of the microorganisms' growth. Some additional water also can appear in fuels as a result of proliferation of microorganisms (see Sect. 5.4).

SEM (scanning electron microscope) and EDS (energy dispersive analysis) results show that the corrosion products formed on the carbon steel coupons both from the naphtha-water and from the gasoline-water mixtures consisted of iron and oxygen. The morphology of the corrosion products (rust) formed in naphtha and gasoline storage tanks is shown in Fig. 5.10.

Thus the main cause of the corrosion in the petroleum product-water mixtures is the presence of water and dissolved oxygen. These data support the electrochemical mechanism of the corrosion of carbon steel in the petroleum products with small

Fig. 5.9 Corrosion of carbon steel in metal/fuel-water environment

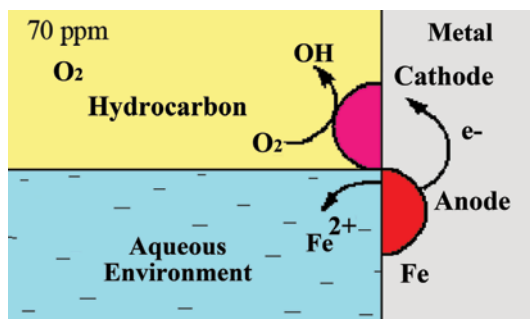


Table 5.2 Chemical composition of the aqueous phase after contact with petroleum products (7 days, T=25 °C). [2]

Parameter	Unit	Deionized water (blank)	Aqueous phase after contact with			
			Gasoline	Naphtha	Kerosene	Gas oil
pH	—	5.8	5.0	5.2	4.8	4.7
Conductivity	μS/cm	0.8	74–205	51–57	38	47–122
Cl ⁻	ppm	0.04	57	2	4	9–13
SO ₄ ²⁻	ppm	0	2	2	1	0.2
NO ₃ ⁻	ppm	0	1–3	2–4	0.04	0.01
HCOOH	ppm	0	3–29	0.6–2.6		
CH ₃ COOH	ppm	0	28–42	7–20		

The chemical composition of the aqueous phase was determined after 7 days of contact with petroleum products while experiencing intensive agitation

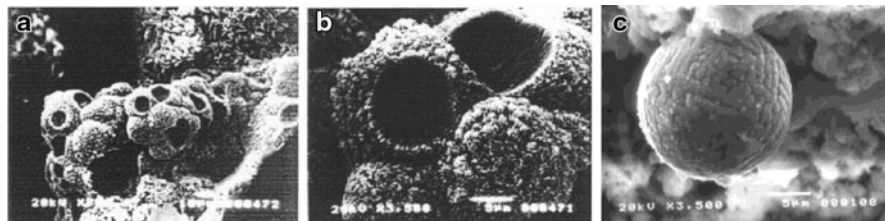


Fig. 5.10 SEM photo of rust formed in naphtha storage tank **a** magnification (×1,000), **b** magnification (×3,500). **c** SEM photo of rust formed in gasoline storage tank magnification (×3,500)

quantities of water. Pitting corrosion was dominant when the water concentration in the naphtha-water mixture was <0.1 %. Above this value, uniform corrosion was more dominant.

The addition of 10 ppm sodium chloride (NaCl) to the aqueous phase of the naphtha-electrolyte mixture increases the corrosion rate of carbon steel by 23 % when 0.1 % electrolyte is added and 73 % when 0.4 % electrolyte is added (Fig. 5.11).

This fact also proves the electrochemical mechanism occurring in the two-phase fuel-electrolyte system. The main recommendation to diminish or prevent corrosion

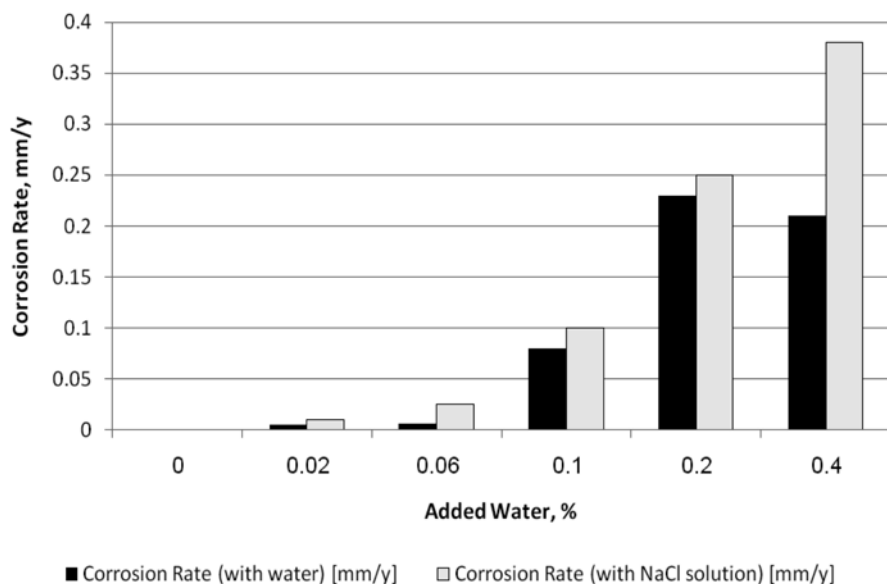


Fig. 5.11 Corrosion rate of carbon steel in naphtha + water mixture with and without 10 ppm NaCl

in petroleum products is to dry them down to values that do not exceed critical water concentrations (see Sect. 7).

5.3.1 Electrical Conductivity of Petroleum Products and Their Corrosiveness

The electrical conductivity of a liquid solution is an ability to conduct electric current by means of ion migration. Electrical conductivity of petroleum products belongs to very important properties because of possible formation of static electricity and influence corrosion of metals. The description of electrical conductivity is given in Appendix G. In this section, electrical conductivity of petroleum products and its influence on metallic corrosion will be discussed.

5.3.1.1 Character of Electrical Conductivity of Petroleum Products

Petroleum products consist of hydrocarbons which do not dissociate into ions under usual environmental conditions. Therefore formation and accumulation of electrical charges in liquid petroleum products occurs as a result of contaminants which are able to form ions. Polar organic compounds and inorganic impurities containing in petroleum products increase their electrical conductivities. Amounts of oxidized

Table 5.3 Specific electrical conductivity (pS/m) of crude oil and petroleum products at 20 °C

Crude oil or petroleum product		Specific electrical conductivity (pS/m) ^a
Gasoline	White spirit	0.02–1
	Naphtha ^b	0.49
	General ^c	0.3–10
	In the pipeline ^{b,d}	5.62
	In the AST ^{b,d}	62.4–71.5
Kerosene	Leaded	> 50
	Avgas	1–30
	General ^c	0.02–50
	Exit from HDS ^b	0.64
	In the AST ^b	1.54
Diesel fuel	Feed to HDS ^b	4.64–6.33
	Jet fuel	0.2–100
	In the pipeline ^b	0.41
	In the AST ^b	0.58
	Low Sulphur <0.05 % S	1–50
	With anti-static additive	50–300
	Gas oil	600–1,200
	Fuel oil	20–3 × 10 ⁵
	Crude oil	10 ³ –10 ⁷

AST Aboveground Storage Tank, *HDS* Hydrodesulphurizer is the process using for removing hydrogen sulphide (H₂S) and other organic sulphur-containing compounds from petroleum products at the oil refineries

^a1 pS/m = 10⁻¹² S/m = 1 CU (see Appendix G)

^bThe values were measured by the author by means of the conductivity meter 1154-00-0001 of the Eence Electronics, Inc. (USA). Accuracy was ±0.5 %

^cReceived at the refinery unit

^dGasoline 95

products (hydroperoxides, peroxides, alcohols, aldehydes, ketones, and organic acids) are increased during storage of petroleum products because of interaction of hydrocarbons with dissolved oxygen. The presence of these substances increases electrical conductivity of petroleum products and can intensify electrochemical corrosion. For instance, purification of kerosene from impurities decreases its electrical conductivity 10–100 times. Electrical conductivity of petroleum products increases with rising of boiling range because the amount of non-hydrocarbon compounds (sulphur-, oxygen-, nitrogen-containing compounds, and compounds with metallic ions) also increases (see Table 5.3).

Small contaminants (mostly uncontrolled) in petroleum products significantly influence their electrical conductivity. Therefore conductivity changes considerably for the same petroleum product in the pipeline or in the storage tank. Significant difference exists between electrical conductivity of kerosene which enters (feeding) (4.64–6.33 pS/m) and exits (0.64 pS/m) the Hydrodesulphurizer (HDS) unit at oil refineries. This fact points out removing organic sulphur-containing compounds from kerosene at the HDS unit. These compounds are responsible for electrical conductivity of kerosene. Electrical conductivity of kerosene in tanks increases 2.5 times

(from 0.64 to 1.54 pS/m) probably because of increase of contaminants entering in kerosene during its transportation from the HDS unit to the storage tank. Electrical conductivities of naphtha (0.49 pS/m) and diesel fuel (0.41–0.58 pS/m) are on the level of electrical conductivity of kerosene after HDS unit (0.64 pS/m). Electrical conductivity of gasoline which is stored in the AST is higher (62.4–71.5 pS/m) and this value can explain partly why gasoline is the most corrosive towards carbon steel among all petroleum products.

The greater electrical conductivity of petroleum products, the larger is a possibility of electrochemical corrosion, but less is a possibility of accumulation of charges of electrostatic electricity. Generally electrical conductivities of gasoline and kerosene are close. For aviation fuels which are transported to airports, this value can raise 10 fold during transportation. Increase of temperature of fuel on 20 °C causes two fold raise of electrical conductivity of fuels.

Water, H₂S, corrosion products and soil dust, ions, phenols, organic acids, and other organic sulphur-, oxygen- and nitrogen-containing compounds dissolved in petroleum products are these contaminants that are responsible for the electrical conductivity of petroleum products. For instance, gasoline usually contains about 80 ppm of water and can dissolve up to 250 ppm of water. Charging takes place at the interface between two substances, for instance, hydrocarbon–metal, or hydrocarbon–polymeric material, or hydrocarbon–water. Separation of electrical charges takes place on the level of ions and polar molecules. This separation is not large when two substances contact without moving, and difference of electric potentials usually is lower than 1 V. When electrical charges are separated as a result of moving one substance against other, the difference of electric potentials increases significantly, to several kilo-volt. It is required small concentrations of water for formation large difference of electric potentials at the surface of phase separation.

5.3.1.2 Criteria Values for Electrical Conductivity of Petroleum Products

Generally all materials (metals, polymers, ceramics, composites, fabrics, suede, paper) and constructions (pipelines, tanks, filters, water separators) contacting with petroleum products are powerful generator of electric charge. Their influence on accumulation of charges of static electricity is even more than velocity and character of pumping of fuels. In order to prevent fires and explosions of petroleum products causing by accumulation of static electricity, should be excluded appearance of a spark discharge in vapor-air space above the fuel and to bring to minimum appeared charge in liquid phase of the fuel. Fuels are not charged if their electrical conductivity less than 1 pS/m. Such fuels are characterized by high purity which is very difficult to reach and keep. Therefore it is very important to specify criteria values for electrical conductivity of petroleum products for prevention static electrical charge formation on the interface liquid petroleum product–metal (or other material). There is no one opinion on this issue. Canadian specification [4] defines the minimum value of electrical conductivity of diesel fuel 25 pS/m; the English

Table 5.4 The electrical conductivity of various liquid media and corrosion rate of carbon steel in them. [1]

Liquid media	Specific electric conductivity at 20 °C, S/m	Corrosion rate of carbon steel ^a , mm/year
Cooling water (industrial) ^b	0.2	0.6–1
Potable water ^c	0.05	0.2–0.3
Demineralised water	10 ⁻⁴	0.1
Gasoline	10 ⁻¹⁰	0.001
Kerosene	10 ⁻¹²	0.0005
Gas oil	10 ⁻¹²	0.0001
Gasoline + 0.02 % wt. water	Two-phase system	0.4
Kerosene + 0.02 % wt. water	Two-phase system	0.5

^aCorrosion rate of carbon steel was determined by the weight loss method with intensive agitation during one week at 25 °C

^bCooling water in the chemical plant (without any treatment by inhibitors, biocides, and anti-scaling agents)

^cPotable water in Israel

document [5]—3 pS/m; and the American standard [6]—50–600 pS/m for jet fuel. For some fuels, electrical conductivities are typically maintained at 150–250 pS/m.

5.3.1.3 Corrosiveness of Petroleum Products

Organic acids, organic sulphur-containing compounds and different ions (for instance, chlorides) are dissolved in small amounts of water containing in petroleum products. In addition to dissolved H₂O and O₂ this is the cause of severe corrosion of carbon steel pipes, pumps, filters and tanks (during filling-emptying operations) when petroleum products move. It is obvious that corrosion depends on electrical conductivity of substances which move (petroleum product–water with other contaminants). The type and concentration of contaminants in petroleum products influences their electrical conductivity. The more electrical conductivity (the less electrical resistance) the liquid has, the higher the ability to carry the electric current on the metal surface between anode and cathode sites, and the corrosion current is consequently more (Eq. 5.7, Sect. 5.1). For example, the electrical conductivity of liquid pure petroleum products is very low, 10⁻¹² S/m, and their corrosiveness is consequently very low, close to zero. The electrical conductivity of pure water is more, 10⁻⁶ S/m, and its corrosiveness is more. Ions H⁺ and OH⁻ are responsible for the electrical conductivity of pure water. Various cations and anions which are present in aqueous solution are responsible for its electrical conductivity. The electrical conductivity of aqueous electrolyte solutions is high, 10⁻³–40 S/m, and they are very aggressive towards metals (Table 5.4). Corrosion rate of carbon steel in gasoline is 100 lower than in demineralized water, but two-fold more than in kerosene and ten-fold more than in gas oil. Thus various petroleum products behave differently regarding carbon steel. We can compare the electrical conductivity of these liquid media. The electrical conductivity of gasoline one million times lower than

that of demineralized water and 100 times more than that of gas oil and kerosene. Small concentrations of water (0.02% wt.) in gasoline and kerosene result in increase 1,000 times of corrosion rate of carbon steel.

Some organic substances containing hetero-atoms (S, O, and N) which are present in petroleum products are responsible not only for their electrical conductivity but also for lubricity and resistance against formation of peroxides. Standard Euro 5 defined concentration of sulphur to 10 ppm in diesel fuel (see Table 1.1). This requirement resulted in introducing of processes of removing sulphur from gas oil (diesel fuel) and kerosene at oil refineries. Together with sulphur, many organic compounds containing nitrogen and oxygen atoms and poly-aromatic compounds also are removed. During hydrotreating (treatment with hydrogen) cyclic organic compounds are removed, which are responsible for electrical conductivity of diesel fuel and kerosene. Thus electrical conductivity of diesel fuel and kerosene drastically diminishes after hydrotreating and can cause generation and accumulation of electrostatic charges (static electricity) which can result in static discharges capable of causing explosions and fires. On other side, corrosiveness of diesel fuel and kerosene also diminishes. Hydrodesulphurization is used for removing hydrogen sulphide (H_2S) and other sulphur-organic compounds from petroleum products at the oil refineries. On the one side, corrosiveness of such petroleum products diminishes. On the other side, low sulphur content in petroleum products can increase microbial contamination and possible MIC.

5.4 Microbial Contamination of Fuels

Chemical components containing in fuels are described in Sect. 1.2.1 and Appendix A. Kerosene (jet fuel) and gas oil (diesel fuel) are sterile when they are first produced because of the high refinery processing temperatures. But they become contaminated with microorganisms during storage and transportation under ambient conditions. First we will describe microorganisms.

A microorganism is a microscopic organism that comprises a single cell, cell clusters, or multicellular relatively complex organisms. Microorganisms include bacteria, fungi (yeasts and molds) and algae which live and proliferate owing to the process named metabolism. Metabolism ('change' or 'outthrow' from the Greek) is the set of chemical reactions that occur in living organisms, including digestion and the transport of substances into and between different cells. In other words, these reactions allow organisms to grow and reproduce, maintain their structures, and respond to their environments. The metabolism of an organism determines which substances it will find nutritious and which it will find poisonous. For instance, some bacteria use hydrogen sulphide as a nutrient, yet this gas is poisonous to animals. Microorganisms are the "simple" representative of life, and they were the first inhabitants on the Earth. Numerous microorganisms live and grow in the environment at pH=0–13, at temperatures between –15 to +150 °C, at pressures up to 1,000 bar, in aqueous solutions with different salt content (from the pure water to the Dead Sea

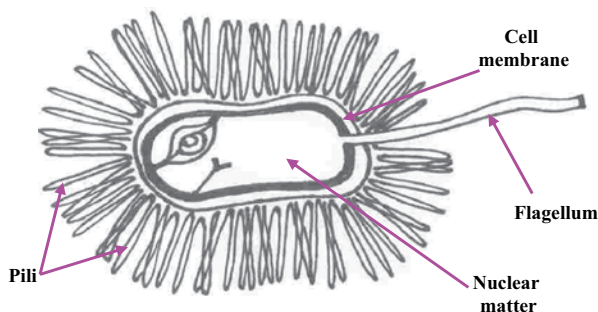
–36% of salts), in oils, in fuels, in soil, in the presence of radiation, and even in the presence of biocides (substances intended for killing bacteria).

Microorganisms are always present in air and water which are the sources of further appearing on our bodies, cloths, tables, walls, and other articles. Similar to that, air containing water vapors and microorganisms can enter into fuels during their storage and transportation. If we retain kerosene and diesel fuel in a container (~100 liter volume) closed by a lid, after a year we can detect slime of grey–brown–black color on the bottom of this container. This is similar to green slime formed on stones in stagnant water or on a glass surface of a vase where flowers with stagnant water are present. The slime formed on the bottom of the fuel container consists of microorganisms and compounds excreted by them. They cling to metal and glass surfaces and can cause erroneous readings in fuel quantity systems, filter clogging, and MIC (see Sect. 5.4.1).

Deterioration of fuels and oxidation of hydrocarbons by microorganisms, and corrosion of metals in the presence of microorganisms are strictly established facts. Microbiological activity depends on the season and is highest in the summer. Therefore microbiological contamination is more prevalent in tropical and semitropical climates because of the more favorable temperature and higher humidity. Temperature change and presence of water is very important factor causing microbial growth in fuels. Microorganisms cannot grow in “pure” (dry) fuels consisting only of hydrocarbons, but they remain “frozen” and viable in such fuels. Microorganisms can distribute themselves throughout the fuel under static conditions. For instance, after 8 days’ incubation, considerable numbers of microorganisms, which were originally introduced into the water layer only, were noted up to 35 cm above the fuel–water interface. Therefore, the microorganisms should have no particular difficulty in contaminating any new water pockets introduced by refueling or condensation. “Frozen” (passive, non-active) microorganisms are waiting for coming good conditions, namely, they are “dormant” like many plants in winter.

Similar to other organisms which need water, microelements, vitamins and proteins, microorganisms also need water and nutrients. Nutrients are chemical substances that organisms need to live, grow, and reproduce. Nutrients are used in organisms’ metabolism which must be taken in from their environment, namely to build and repair tissues, regulate body processes, and are converted to and used as energy. For instance, the chemical elements humans consume in the largest amounts are carbon, hydrogen, nitrogen, oxygen, phosphorous, and sulphur. It is interesting that microorganisms need similar nutrient elements which exist in fuels. In addition, nutrients include inorganic salts and some metal ions. Water, air, dust, microbial byproducts, various materials (metallic components, polymeric materials, even people) may be the sources of nutrients for bacteria. Microorganisms also need electron donors (inorganic or organic substances releasing electrons), and acceptors (molecules or ions which can obtain electrons, e.g., oxygen (O_2), carbon dioxide (CO_2), nitrates (NO_3^-), sulphates (SO_4^{2-}), or ferric ions (Fe^{3+})). These substances can be present in small and enough amounts in fuels for the growth of microorganisms. Large diversity of microorganisms exists according to their metabolism:

Fig. 5.12 Structure of a bacterium. [1]



various sources of energy (light or chemical substances), carbon (CO_2 or organic substances), electron donors and electron acceptors. However, the common is that they all need water.

The dimensions of most microorganisms are about 1–10 μm length and 0.2–1 μm in diameter. Microorganisms are very light, therefore they move with aerosols (tiny solid or liquid particles suspended in the air) from one place to another, form deposits on metallic equipment and structures in air, water, soil, crude oils, fuels, and can exist for a long time without food (nutrients). Many species of bacteria swim in liquids by means of *flagellum*, i.e., hairlike structures whose whiplike lashing provides propulsion (Fig. 5.12). Motile bacteria can swim towards a higher concentration of a nutrient. Living organisms are unique in that they can extract energy from their environments and use it to carry out activities such as movement, growth, and reproduction. When applied to bacteria, the term growth is identified with development and reproduction, and refers to an increase in the number of bacteria in a population rather than in the size of an individual microorganism. Bacteria usually reproduce through binary fission, budding, chains of spores, and through the segmentation of elementary units, shortly, in asexual processes, in periods lower than 20 min. A single cell and its descendants will grow exponentially to more than 2 million cells in 8 h. This growth rate is never actually realized because microorganisms are limited by space and available nutrients. They are defined by means of an optical microscope. A large quantity of microorganisms form *biofouling* (*biofilm*) defined with the naked eye, and they are slippery to the touch. They choose metal surface as a place to live and form biofilms with thicknesses from several microns to several centimeters.

Microorganisms do not need dissolved but free water in fuels. Without free water there is no microbiological growth in fuels. Water content for microbiological proliferation in fuels is critical. If we remove any free water, growth of microorganisms ceases, even can be stopped. Thus, microorganisms can grow only in the presence of free water in crude oil, fuel oil, gas oil (diesel fuel), kerosene (jet fuel), and biodiesel.

Although microbial contamination occurs in a wide range of fuels, some fuels have been found to be more susceptible than others. For instance, straight chain alkanes (paraffins) tend to be more readily degraded by microorganisms than aromat-

ics and alkenes (olefins). Really, microorganisms do not grow in gasoline, because gasoline contains ~25 % olefins and ~35 % aromatics, and probably, because microbes consume hydrocarbons of higher molecular weight than that which are present in gasoline.

Use of hydrocarbons by microorganisms for their growth is called biodegradation of hydrocarbons and was firstly described probably by M. Miyoshi in 1895. The amount of water required for microbial growth is small. In addition to free water another source of water in fuels is that water is a product of the microbial degradation of hydrocarbons. Since most microorganisms need free water to grow, microbial growth usually occurs at the fuel-water interface. Thus microorganisms live in water, use certain hydrocarbons and nutrients on the water-fuel boundary and generate water for further proliferation. For instance, fungi *Cladosporium resinae* grew in 80 ml water per liter of kerosene and after a month, the amount of water increased more than ten-fold.

In relation to surviving in the presence of oxygen, three types of microorganisms exist. The first type needs air (more precisely, oxygen) to grow; they are named *aerobic*. The second type can grow only in the absence of air; they are named *anaerobic* and usually they find their place under aerobic conditions which isolate them from oxygen. The third type is most survived, can exist both in the absence and presence of air; they are named *facultative* microorganisms.

Aerobic microorganisms use oxygenase enzymes which require oxygen in order to function. Under anaerobic conditions, nitrate or sulphate reducing, or methanogenic microorganisms use various hydrocarbons, mainly, cyclic aromatic compounds such as benzene, toluene, xylene, methylbenzene, and naphthalene. The degradation rate of hydrocarbons is 50–70 times higher in the presence of oxygen than that under anaerobic conditions. We can use aeration as the method of inactivation of anaerobic microorganisms, and create conditions without air (oxygen) against aerobic microorganisms.

We can sum up that water, oxygen (presence or absence), nutrients, electron donors and electron acceptors are indispensable sources under suitable temperature for microorganisms' growth in fuels.

If detergents (surfactants) are present in fuels, they increase the bioavailability of hydrocarbons and emulsify ("bring into solution") nonpolar hydrophobic compounds for use by microorganisms. It is very interesting to emphasize that a similar process occurs during desired bioremediation in soil and water for their purification from hydrocarbon (fuel) contamination. During biodegradation of fuels, microorganisms can synthesize bio-detergents, which increase their access to hydrocarbons. There is wide diversity of number and composition of hydrocarbon degrading microbes. About 30 types of bacteria, more than 80 types of fungi and more than 12 types of yeasts were found in fuels. Only 20–40 % of these microorganisms are capable of using hydrocarbons for their proliferation. Microbial metabolism may lead to the production of various organic compounds such as aldehydes, fatty acids, mercapturic acid, phenolic compounds (i.e., catechol), dihydro-diol, epoxy, vinyl chloride, and 1,2-dichloroethene. Many of these compounds are regarded as toxic or carcinogenic substances. All these compounds can deteriorate fuels and influence

corrosion processes. Unfortunately we know very little about the environmental impact of these compounds.

Special problems can exist with microbiological growth in aircraft fuel systems because it causes fouling of filters, fuel screens, and erratic operation of fuel-quantity probes (capacitance probes), as well as the corrosion of fuel tanks made from aluminum.

Hydrocarbon utilizing microorganisms, mostly *Cladosporium resinae* and *Pseudomonas aureginosa*, are called HUM bugs and can be present in jet fuel. They live in the water-fuel interface of the water droplets, form dark-black-brown-green gel-like mats, can consume polymers and cause corrosion because of their acidic metabolic products (see Sect. 5.4.1). They are also sometimes incorrectly called *algae* due to their appearance. Anti-icing additive Di-EGME retards their growth (see Sect. 2). There are about 250 kinds of microorganisms that can live in jet fuel, but fewer than a dozen are really harmful.

The results of microbial contamination in three pipelines and three aboveground storage tanks containing kerosene in service are shown in Table 5.5 and in Fig. 5.13.

Five types of microorganisms were examined: anaerobic, aerobic, fungi, SRB (Sulphate Reducing Bacteria), and iron bacteria. The data showed that anaerobic and aerobic microorganisms existed both in pipelines and tanks at all levels of height, and their concentration is more than the dangerous allowable value of 10^3 – 10^4 microbes in 1 ml of kerosene. Such values show significant proliferation of microorganisms in kerosene during its transportation and storage. The value of 10^3 microbes in 1 ml of kerosene shows the presence of potential quantity of microorganisms for proliferation, namely, they will grow in the presence of sufficient amount of water and nutrients. Type of microorganisms and their concentrations depend on the sample position. Kerosene in pipelines is contaminated less (10^3 – 10^4 microbes in 1 ml of kerosene) than in tanks but has potential for proliferation of microorganisms in the presence of water. Contamination by microorganisms increases from the top to the bottom of the tanks, and their highest quantity is in the drain water (bottom). Upper and middle parts of kerosene tanks have microbial contamination similar to that in the pipelines (10^3 – 10^4 microbes in 1 ml of kerosene). SRB and iron bacteria are absent in pipelines, in upper and middle parts of the tanks. It is important to emphasize that: aerobic and anaerobic microorganisms are present in similar amounts (10^7 – 10^8 microbes in 1 ml of kerosene); fungi are present in small amounts (~ 100), commonly found in kerosene; SRB and iron bacteria are present in large quantities ($\sim 10^6$) only on the bottom of the tanks. In spite of the similar dimensions of the three kerosene tanks, microbial contamination is different in them. The kerosene in the tank A is relatively pure in comparison to that in the tanks B and C. Certainly all tanks are not in identical service conditions. The data in Table 5.5 show that strict periodical control of presence of microorganisms in pipelines and storage tanks and of course periodical cleaning from sludge are required. It is desirable to examine the presence of microorganisms at least once a month, to drain water from tanks once a week (sometimes every 3–4 days; the period depends on the rate of water appearance and its accumulation and the level of contamination), and to clean the bottoms from sludge in accordance with the level of sludge (it is desirable every 4–5 years).

Table 5.5 Microbial contamination (CFU^a/ml) of kerosene in pipelines and aboveground storage tanks

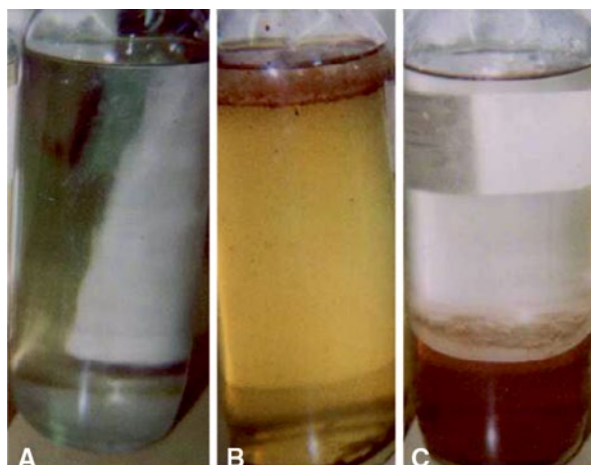
Sample Position			Anaerobic TPC	Aerobic TPC	Fungi	SRB	Iron bacteria
Pipeline ^b			$(3-7) \times 10^4$	$(0.3-1) \times 10^4$	10	0	0
Aboveground Storage Tank	A	Top	6.0×10^4	1.4×10^3	0	0	10
		Middle	5.0×10^4	8.0×10^3	200	0	0
		Bottom	4.0×10^5	1.0×10^4	70	0	800
	B	Top	2.0×10^5	2.0×10^4	350	0	0
		Middle	2.0×10^5	3.3×10^5	50	0	0
		Bottom	3.7×10^7	8.0×10^7	0	150	6.0×10^4
	C	Top	4.0×10^5	4.0×10^4	200	0	0
		Middle	3.0×10^5	2.6×10^4	50	0	0
		Bottom	8.0×10^7	1.6×10^8	500	1.0×10^6	5.1×10^5

A, B, C are the three different tanks. The height of each tank is 12.8 m; the diameter is 23.8 m; the volume is 5,700 m³. *Top* the upper level of kerosene in the tank, *Middle* the center of the tank; *Bottom* the lower part of the tank (drainage). *TPC* Total Plate Count, *SRB* Sulphate Reducing Bacteria

^aCFU/ml Colony-forming units per milliliter of liquid; an estimate of viable bacterial or fungal numbers

^bAverage from the three pipelines

Fig. 5.13 Samples from the bottoms (drainage) of the three kerosene storage tanks A, B and C (see Table 5.5). We can see microbial contamination at the interface water–kerosene in the tanks B and C.



We should emphasize some other factors influencing microbial contamination, for instance, the duration and conditions of fuel storage. If there is a low turnover of a stored fuel, such as in strategic reserve, contamination is much more likely to develop. Poorly maintained or outdated storage facilities also present greater opportunities for contamination. In some cases, in addition to the microbial contamination at the fuel-water interface there is the sessile population attached to the tank wall surface. This is frequently overlooked. Unless treated it will act as inoculums place for future contamination of fuels.

5.4.1 Microbial Contamination of Biodiesel

Certain organic sulphur-containing compounds (thiophenes, thiols, thiophenic acids, and aromatic sulphides) containing in conventional diesel fuels are natural biocides. Biodiesel is hygroscopic, absorbing water from the atmosphere. Mono- and diglycerides left over from the reactions to produce biodiesel can act as emulsifiers, facilitating formation of persistent emulsions. Sometimes tankers transporting biodiesel are exposed to seawater in compensated fuel ballast systems. During refueling, biodiesel displaces the seawater, but some of water remains. Certain microorganisms are naturally occurring in biodiesel; others are introduced from air or water. As water is more soluble in biodiesel than in conventional diesel fuel, the former is more susceptible to biological contamination, growth of microorganisms, biofouling and MIC. Types of surviving microorganisms depend on hydrocarbon composition. Anaerobic microorganisms (usually SRB) are active in sediments on tank bottoms and cause severe localized corrosion. These sediments look like black sludge biomass and by the way can be used as feedstock for producing biodiesel. Biodiesel is especially susceptible to degradation by certain microbial species (for instance, *Sphingomonas* spp.) and they accelerate MIC. Biodiesel even may degrade more quickly than conventional diesel fuel. Since the biocides work where the HUM bugs live (in aqueous phase), biocides that are used with conventional diesel fuels usually work equally well with biodiesel. Microbial contamination does not occur if all system containing biodiesel is clean and dry. Thus precautions to prevent water contamination in biodiesel is even more important than in conventional diesel fuel, namely, good storage tank maintenance, fuel/water separators on the truck, and use of water vapors absorbents.

5.4.1.1 Consequences of Microbial Contamination of Fuels

Once a microbial population becomes established above some value (usually $> 10^3$ – 10^4 microbes in 1 ml of a fuel) and free water is present, it may result in deterioration of fuel quality, haziness, formation of sludge, degradation of fuel additives, filter plugging, appearing of odor, and corrosion.

Deterioration of fuel quality change of density, distillation boiling range, color, cetane number (for diesel fuel), sulphur content, copper corrosion, etc.

Fuel haziness The cause of haziness is an increase of water content in the fuel resulting from the production of biosurfactants. These are by-products of microbial growth (secreted by microorganisms) and alter the surface tension at the fuel-water interface. As a consequence the solubility of water in the fuel is increased. Fuel haziness is a clear indication that fuel is out of specification.

Formation of sludge Microorganisms, the products of their metabolism, wastes and debris are deposited on the tank bottom where they form a layer of sludge (slime or mats) called biofouling. Surfactants cause formation of stable slime. It is not

necessary that surfactants be present for microorganisms to flourish, but they promote luxuriant growth by aiding the mixing and emulsifying of fuel and water. This sludge creates an environment which favors MIC.

Degradation of fuel additives Certain additives, especially those rich in nitrogen and phosphorous, encourage microbial growth as microorganisms use them in metabolism. Thus the additives are degraded and consequently their effect is lost.

Filter plugging Biopolymers (known as extracellular polymeric substances, EPS) are formed during microbial growth. They are high molecular weight organic compounds secreted by microorganisms into their environment. These are gummy products which, along with microbial and other debris, are deposited on filters and pipes leading to reduced flow rates and blockages. At end user level this can have serious consequences causing engine damage and in extreme cases complete failure.

Appearing of odor This is principally as a result of hydrogen sulphide production by SRB.

Corrosion (see Sect. 5.4.2).

5.4.1.2 Prevention of Microbial Contamination of Fuels

The best struggle with microbial contamination of fuels is prevention. And the most important preventive step is keeping the amount of free water in fuel storage tanks and aircraft fuel tanks as low as possible. It is recommended to install desiccant breathers with one-micron filters on them. Desiccant breathers help prevent moisture and other contaminants from getting into tanks, and also help keep the air above the level of the fuel dry. It is recommended monitoring the fuel and free water at the bottom in storage tanks regularly for the presence of free water and to test it for microbial growth. These preventive measures are far better than having to resort to chemicals to kill microbial growth in tanks. Since 1956, when fuel system malfunctions in the aircraft were traced to microbial sludge formation, *biocides* (as fuel additives—see Sect. 2) have been developed which would retard the growth of microorganisms, and the same time, be compatible with the fuel system components. All biocides have different effectiveness, potency and duration of biocidal activity. More accurately, we have to call biocides according to their anti-microbial activity, *bactericide*, *fungicide*, and *algicide*. All existing biocides are divided into oxidised and non-oxidised types, and work by two ways. Some biocides change the penetrating properties of the bacterial cell membrane, and as a result disturb the metabolic processes (interchange between proteins), so important for bacteria's life. Other biocides fully destroy the membrane, or prevent the entry of nutrients into and the outlet of wastes out of the cell. Only approved biocides may be used under controlled conditions (see Sect. 2 and 7.5). Biocides have drawbacks. The treatment with biocides may improve the state of contamination by microorganisms and prevent biofouling formation but most biocides are toxic, presenting risks to employees and the environment.

5.4.2 *Participation of Microorganisms in Corrosion of Metals in Fuels*

Microbiologically influenced (or induced) corrosion (in short, MIC) is corrosion which takes place with the participation of some special kinds of microorganisms on a surface of metals under particular conditions. ‘Participation’ means the presence (for instance, creation differential aeration cells) or activity (or both) of microorganisms in biofilms on the surface of the corroding material.

MIC occurs on inner surface of the bottoms of storage tanks containing crude oil, gas oil (diesel fuel), kerosene (jet fuel), and fuel oil (Figs. 5.14–5.17).

The external surface of the tanks and pipelines that are in contact with the soil also can be affected by MIC (Fig. 5.17).

Like not all bacteria which are present in the human body can cause illnesses, not all bacteria on a metal surface can give rise to MIC. Only special kinds of bacteria result in MIC. There are found several hundreds types of bacteria and fungi that decompose organic components of crude oil and fuels. Some bacteria can break down fuel additives (among them corrosion inhibitors), reducing their effectiveness. Nearly there are no metals and alloys which are resistant to MIC. It is not easy to identify that corrosion occurs due to bacterial activity because the results are pits of various forms associated with chloride or oxygen attack, existence of differential aeration cells (under deposit corrosion), crevice or galvanic corrosion. Therefore prior to recognition of MIC, we should examine other corrosion types and mechanisms. Usually MIC occurs in combination with other types of corrosion which complicate its determination. In any case, how can we prove MIC in tanks containing crude oil and fuels? First, inner surface of bottoms is covered by sludge (slime, biofouling, biofilm). Bacteria in biofilm excrete *extracellular polymeric substances* (EPS), or sticky polymers, which work as glue and hold the biofilm together and cement it to the metal surface. EPS serves for trapping and concentrating nutrients from the environment, and acts as a protective coating for the attached cells, and protect microorganisms from biocides and other toxic substances. Because EPS holds a lot of water, a biofilm-covered metal surface is gelatinous and slippery. More than 99% of all microorganisms live in biofilm communities. Microorganisms adhere to carbon steels, aluminum, stainless steels and polymers with almost equal “enthusiasm” within 30 s of exposure. The material of the surface where biofilm is attached has little or no effect on its growth.

The black biofilm layer can be present on bottoms of tanks containing crude oil and fuel oil. Grey, black and greenish layers can be present on bottoms of tanks containing kerosene (jet fuel) and gas oil (diesel fuel). We can detect such slime on the bottom of a barrel (open to the atmosphere) containing gas oil (diesel fuel) after a half a year.

Then it is necessary to check the presence of specific microorganisms responsible for corrosion. There is no accepted classification of microorganisms inducing

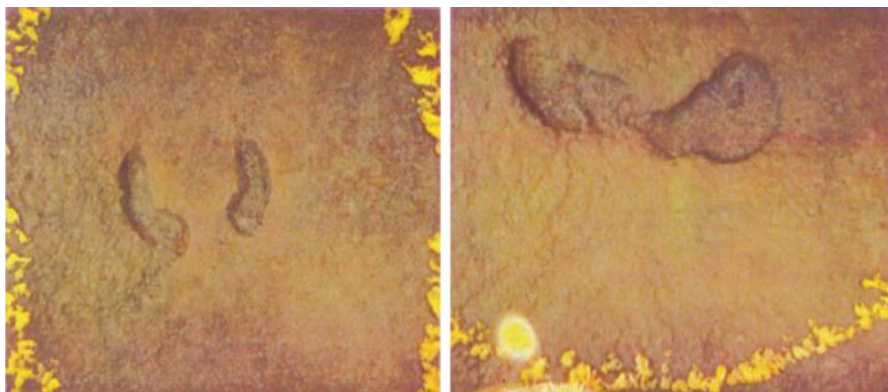
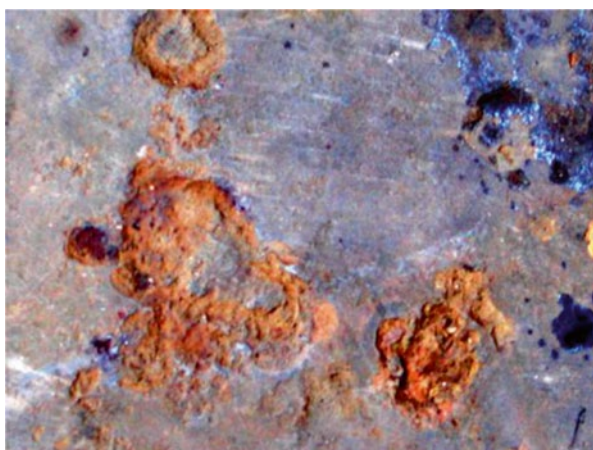


Fig. 5.14 Pits formed on inner surface of the bottoms of the AST containing crude oil as a result of MIC (18 years of service)



Fig. 5.15 Holes formed on inner surface of the bottoms of the AST containing crude oil as a result of MIC (20 years of service)

Fig. 5.16 Shallow pits formed on inner surface of the bottoms of the AST containing fuel oil as a result of MIC (15 years of service)



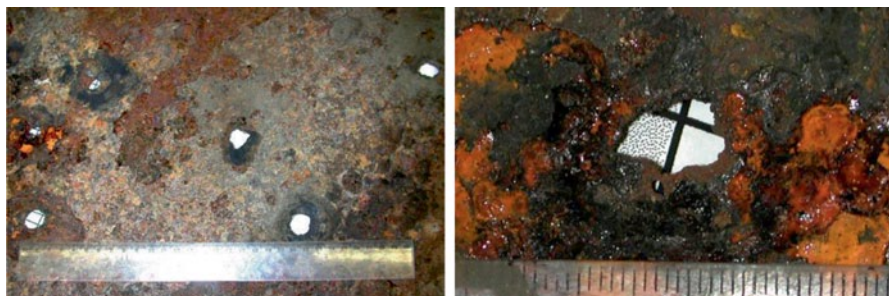


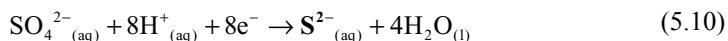
Fig. 5.17 Holes formed on outer surface of the bottoms of the AST containing crude oil as a result of MIC (20 years of service)

corrosion. It is convenient to divide all microorganisms taking part or influence corrosion into five groups:

- a. *Sulfate Reducing Bacteria* (SRB).
- b. *Microorganisms producing acids*.
- c. *Microorganisms oxidizing ferrous (Fe^{2+}) and manganese (Mn^{2+}) cations*.
- d. *Slime-forming bacteria*.
- e. *Methane (methanogens) and hydrogen producing bacteria*.

They may be *anaerobic*, *aerobic*, or *facultative* (see Sect. 5.4).

A. Sulfate Reducing Bacteria (SRB) are anaerobic and the most distributed in nature and in industrial systems. They exist in crude oils, in fuels, in water, in soil, and in wastes. SRB were historically the first microorganisms which were found to be responsible for corrosion of carbon steel (1910, Gains R.H.) and cast iron tubes in soil (1934, Wolzogen Kühr and Van der Vlugt). SRB accelerate the reducing of sulphates (SO_4^{2-}) contained in soil (or in aqueous solution at the tank bottom) into sulphides (S^{2-}) which attack metals:



It is more correct to call them by *sulphide generating bacteria*. At the beginning, ions H^+ accept the electrons from the iron and form neutral atoms H. Then these H atoms reduce ions SO_4^{2-} to S^{2-} . Sulphides forming in this process are corrosive to many metals, especially to iron, copper, zinc and their alloys. Usually SRB proliferate under aerobic or heterotrophic bacteria in the absence of air, best at temperatures from 25 to 35°C. They are widespread on the bottom of crude oil and fuel storage tanks (Fig. 5.18). Iron sulphides as corrosion products forming under SRB biofilm on steel surface have black color. If several drops of hydrochloric acid (15 wt%) are poured on black corrosion products, it would smell of rotten eggs, a specific smell of hydrogen sulphide evolved as a result of the reaction of iron sulphide with hydrochloric acid:



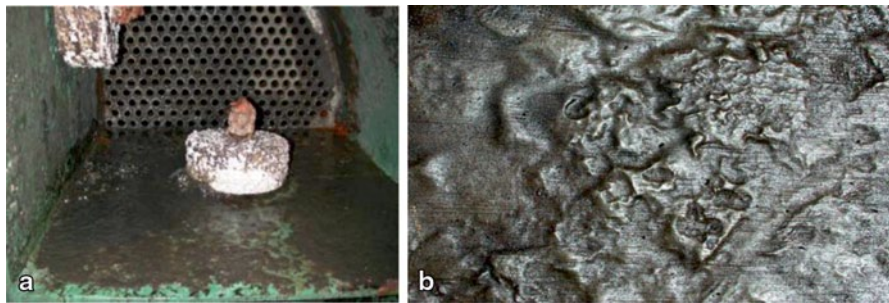


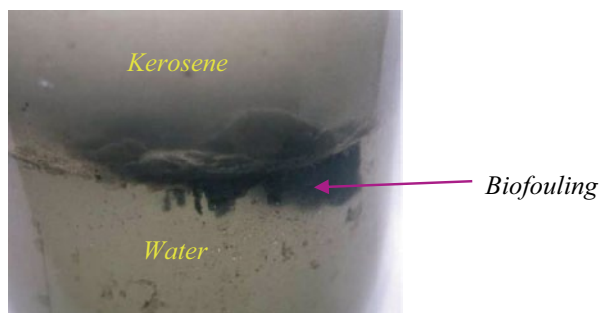
Fig. 5.18 **a** SRB formed in heat exchanger (4 years). **b** Corroded carbon steel bottom of the crude oil aboveground storage tank after 18 years of service as a result of SRB activity. [1]

A simple agitation or flushing of media may kill SRB and prevent their dangerous attack. Mechanical cleaning (scrubbing and scraping) of sludge is also an effective method. One way to restrict the SRB activity is to reduce the concentration of their essential nutrients: phosphorus, nitrogen, and sulphate-containing compounds.

B. Microorganisms producing acids Usually these microorganisms are heterotrophic bacteria and fungi, sulphur oxidizing bacteria, and bacteria oxidizing ammonia (NH_3) to nitric acid (HNO_3). These microorganisms play essential role in corrosion of metals in crude oil, fuels, soil, and water.

Heterotrophic (facultative) bacteria and fungi They are both aerobic and anaerobic bacteria that use organic (carbon-containing) compounds as a source of energy and carbon. This characteristic distinguishes heterotrophic bacteria from chemoautotrophic (chemosynthesizing) and photoautotrophic (photosynthesizing) bacteria, which assimilate CO_2 as a source of carbon. There are particular heterotrophic bacteria capable of decomposing hydrocarbons, phenol, and other components of fuels. MIC which was caused by heterotrophic bacteria and fungi firstly was reported in aircraft. Severe pitting corrosion was revealed in jet aircraft fuel tanks made of aluminum in the beginning of 1950s. The fuel systems in the airplanes were made of aluminum alloy, and jet fuel was stored inside. It was difficult to believe that jet fuel consisting of hydrocarbons, non-corrosive towards metals, was responsible for such pits. Biological filaments were found on the aluminum surfaces inside the fuel systems. Microbiological analysis showed the presence of fungi *Hormoconis resinae* (formerly known as *Cladosporium resinae*). These filamentous fungi excrete organic acids, not so strong as inorganic acids, but they were strong enough to cause the pitting corrosion of aluminum. The question was how did these fungi appear and proliferate in jet fuel? We said that microorganisms might be present, but not be active (not be reproduced, dormant) in any environment: air, fuel, water, solid materials, etc. The fungi might enter into the fuel storage system with air through the vents. Kerosene (jet fuel) manufactured at oil refineries usually contains a very small quantity of dissolved water, about 30–80 ppm. Fungi can not grow in jet fuel without water, but such small water concentrations are not enough for their proliferation. Dissolution of water in jet fuel depends on temperature and relative

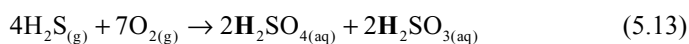
Fig. 5.19 Microorganisms forming biofouling at the water–kerosene interface (this mixture was taken from a kerosene storage tank)



humidity of air (see Sect. 1.2.1.1). During the airplanes' flights and day-night cycles temperatures changed, air containing water vapors ingressed into the fuel system through the vents or broken and unseated gaskets in the caps, and then water vapors are condensed. This water can absorb hydrocarbons contained different additives (some of them high affinity to water). When the quantity of water is enough to be separated from jet fuel, a two-phase water–jet fuel medium is formed. Dissolved oxygen is present in both hydrocarbon and water phases. Now water (“home” for fungi growth) and jet fuel (hydrocarbons are food for their growth) are present in separate phases at suitable temperatures and aeration. Growth of microorganisms in fuel storage tanks occurs at the water–hydrocarbon boundary and biofouling is formed (Fig. 5.19). For instance, fungi were detected in 80% of jet fuel samples from aircraft tanks in the USA, Australia and England. Metabolic by-products of these fungi are such organic acids as oxalic, lactic, and acetic (pH=3–4). Aluminum is resistant to acetic acid, thus other organic acids cause pitting corrosion of aluminum. Usually *Hormoconis resinae* do not exist alone, but together with various aerobic and anaerobic bacteria.

Fungi and heterotrophic bacteria may deteriorate not only jet fuel, but also diesel fuel and lubricating oils if they have slight water contamination. The fungi can form dense fungal *mats* causing operational problems (filter blockage, etc.). Such *biofouling* can also consume rubber gaskets, O-rings, and rubber hoses. The food cycle of the fungi releases more water into the system, which in turn favors an increase in fungal growth. Thus, the corrosive bio-environment is self-perpetuating.

Sulphur oxidizing bacteria They are aerobic bacteria deriving energy from the oxidation of elemental sulphur and its compounds (for example, hydrogen sulphide, or other sulphur-containing substances) to sulphates (SO_4^{2-}):



Sulphur is present in nature as molecules containing eight atoms (see Appendix B, Table B.1). Aerobic sulphur oxidizing bacteria usually live in soils. They are

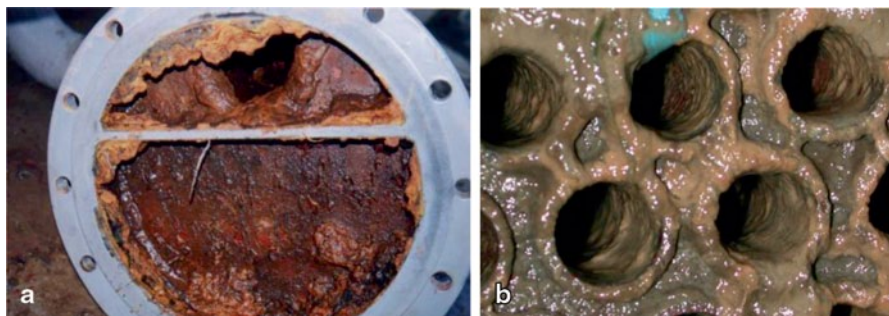
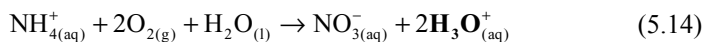


Fig. 5.20 **a** Iron bacteria. **b** Slime-forming bacteria

responsible for acid mine drainage, proliferate inside sewer lines, and when produce sulphuric acid (up to 10 wt%), are very dangerous to steels, copper, aluminum, zinc, in short, to all materials (concrete, reinforcing steel, some coatings) non-resistant to acids. Sulphur oxidizing bacteria are almost always accompanied by SRB. Underground storage tanks and pipelines can be attacked by these microorganisms.

Bacteria oxidizing the ammonium cation (NH_4^+) to nitric acid (HNO_3) They are bacteria which use the ammonium cation (NH_4^+) as food and oxidize it to nitric acid (HNO_3):



This acid may attack many metals, alloys, concrete, polymers, and coatings. Ammonia and its salts are widely used in fertilizers and agricultural fields are the source of food for bacteria giving rise to severe corrosion of underground storage tanks, pipes and other metallic constructions.

C. Microorganisms oxidizing cations Fe^{2+} (iron bacteria) and Mn^{2+} . They are the bacteria that derive the energy they need to live and multiply by oxidizing dissolved ferrous (Fe^{2+}) and manganese (Mn^{2+}) cations to Fe^{3+} and Mn^{4+} , respectively. In the first case, the resulting rust (ferric hydroxide FeOOH and ferric oxide Fe_2O_3) appears as insoluble reddish-brown slime. Therefore, they also are called *iron-depositing*, *iron*, or *iron-oxidizing bacteria* (IOB). They can proliferate in waters containing as low as 0.1 ppm of iron, and at least 0.3 ppm of dissolved oxygen is needed for oxidation. Iron bacteria can exist in drainage water in fuel storage tanks and soil but mostly are responsible for severe corrosion in water cooling systems, drinking water pipes, water extinguishing lines, and fire sprinkler systems (Fig. 5.20a).

D. Slime-forming bacteria Fungi and algae belong to facultative microorganisms that can exist and grow both in the absence and in the presence of air. These microorganisms live and grow well in many media, produce extracellular polymers that make up slime biomass (biofouling). This polymeric mat is actually a sophisticated network of sticky strands that bind the cells to a metal surface (Fig. 5.20b).

Slime-forming bacteria use various organic substances (hydrocarbons from fuels, as well as contaminants in soil and water) as food. They influence corrosion in two ways: forming *differential aeration cells* (and as a result, cause localized corrosion) and excreting organic acids (oxalic, lactic, acetic, and citric). Therefore they also appear to be *microorganisms producing acids*. Many metals and alloys, concrete, and polymeric materials undergo attacks from these acids. Slime-forming bacteria can be efficient “scrubbers” of dissolved oxygen, thus preventing the oxygen from reaching the underlying surface. This creates an ideal site for the growth of SRB and other anaerobic microorganisms. Some particular enzymes existing within polymeric masses are capable of intercepting and breaking down toxic substances (biocides) and converting them into nutrients for other types of microorganisms. Sometimes the use of biocide may even result in a proliferation of microorganisms. We observed such effect when the slime at the bottom of the kerosene storage tank was treated with hypochlorite (efficient biocide in many systems!). After a short period of decrease in the quantity of microorganisms, their intensive growth (more severe than previously!) occurred. In these cases, only mechanical cleaning from slime-forming bacteria may help in the prevention of MIC.

Sometimes MIC occurs even before filling the aboveground storage tank (AST) by fuel. Usually hydrotest is carried out for examination of hermeticity of erected new AST. We will describe the case of *MIC of floating roofs and pontoons made from aluminum alloy Al 5052 during hydrotest*. The 3,000-m³ tanks were made of carbon steel. Test water came from the fire water piping without any pretreatment. The tanks were filled and exposed to ambient temperatures ranging from ~12 °C (night) to 25 °C (day) for 3 weeks. The floating roofs and pontoons were inspected following water drainage. Visual observation revealed that a remarkable amount of white corrosion products had formed on the underside of the roofs and pontoons (Fig. 5.21). The entire roof and pontoon surface in contact with the water suffered severe localized corrosion. Shallow and deep pits, and even holes, were found under the white deposits.

The investigation revealed that the strong localized corrosion of the aluminum alloy Al 5052 floating roofs and pontoons that occurred during hydrotesting was directly related to the activity of microorganisms (Table 5.6). Aluminum alloy Al 5052 contained magnesium (2.2–2.8 wt%) (see Appendix H).

Table 5.7 shows the chemical composition of fire water used for the hydrotest.

Microbiological analysis showed the presence of various corrosion-inducing microorganisms (aerobic, anaerobic, slime-formers, SRB, IOB, and fungi). Concentration of these microorganisms in the corrosion products was two to four orders of magnitude higher than in the water, indicating a significant biofouling process. The environmental conditions (temperature, chemical composition of water, and stagnancy) were favorable to the accumulation and fast proliferation of water microflora on the roof and pontoon surface in tank during hydrotest. No corrosion attack occurred in the same water after filtration-sterilization (0.45-μm nominal pore size). Corrosion tests conducted in both water types (original and sterilized)



Fig. 5.21 Pontoon made from aluminum alloy Al 5052 after a 3-week hydrotest

Table 5.6 Microorganism enumeration in fire water and corrosion products

Microbial group type	Fire water (CFU ^a /ml)	Corrosion products (CFU ^a /g)
Heterotrophic aerobic bacteria	2.4×10^3	2.2×10^7
Heterotrophic anaerobic bacteria	5.1×10^3	4.5×10^7
Sulphate Reducing Bacteria (SRB)	4	6.7×10^2
Iron-oxidizing bacteria (IOB)	4	1.4×10^4
Fungi (total plate count)	1.7×10^2	8.0×10^6

^aColony-forming units (viable cells)—unit of measurement of microorganisms

Table 5.7 Chemical content of fire water

Parameter	Unit	Value
pH	—	7.6–8.2
p-alkalinity	ppm CaCO ₃	2–40
Total alkalinity	ppm CaCO ₃	150–200
Chlorides (Cl ⁻)	ppm	400–630
Sulphates (SO ₄ ²⁻)	ppm	60–180
Total hardness	ppm CaCO ₃	250–300
Calcium hardness	ppm CaCO ₃	110–160
Magnesium hardness	ppm CaCO ₃	130–140
Iron	ppm	0.5–16
Oil	ppm	1
Nitrates (NO ₃ ⁻)	ppm	10
Total Organic Compounds	ppm	3
Conductivity	μS/cm	900–1,300

demonstrated that aluminum-magnesium alloy Al 5052 is much more susceptible than pure aluminum Al 1100 to MIC. Countermeasures are recommended in such cases.

- Consideration should be given to water quality used in hydrotests.
- Prior to a hydrotest, water must be filtrated by means of biological filters.
- Corrosion inhibitors must be used.

5.4.2.1 The Prevention of MIC in Fuel Systems

We should remember that it is better to prevent MIC in fuel systems than to combat. We also should control situation and examine fuels and drain water from storage tanks on microbiological contamination. We will describe main preventive measures against MIC in fuel systems.

- a. *Technological measures, or changes of conditions in the system* (see Sect. 5.4). Drainage and cleaning of tanks bottoms are very useful technological measures against MIC inside tanks. There are no general guidelines for the implementation of drainage, but it is recommended to perform at least once at 3–4 days. The frequency of drainage may be reduced or increased according with formation and accumulation of water in the bottom. Mechanical scrubbing or scraping, and high pressure spraying are also used. It is recommended to do this every five years or when heavy thick fouling is formed in the bottom.
- b. *Use of coatings*. The inner side of storage tank bottoms for crude oil, kerosene (jet fuel), gas oil (diesel fuel), and fuel oil must be coated (see Sect. 7.2 and Appendix L). The inside of pipes may also be coated.
- c. *Change of metallic constructions for non-metallic materials* (polymers, fiberglass, and concrete). However, acid-producing bacteria are very dangerous to concrete, some polymers, and fiberglass.
- d. *Filtration*. Microorganisms range in size from 0.2–2 μm in width or diameter, and up to 1–10 μm in length for the nonspherical species. Therefore fuel deteriorated with them may be filtrated through *biological* filters with porosity (pore dimension) of 0.2 μm . Because of very small pore dimensions, the flow rate of fuel is very low, and much time is needed to treat media deteriorated by microorganisms. Certainly, if large volumes of fuels are used, filtration through *biological* filters is not cost-effective.
- e. *Use of ultraviolet (UV) light and ultrasound (sonication)*. These methods are used to kill microorganisms in water and did not find application in fuel systems.
- f. *Cathodic protection* (see Sect. 7.3). In order to protect carbon steel constructions in an aqueous solution of electrolytes (or in soil), from the thermodynamic point of view, the electric potential must be lower than -0.85 V regarding the copper-copper sulphate reference electrode. The presence of microorganisms in the electrolyte environment (cathodic protection works only in electrolytic solutions) needs diminishing of this protective potential lower than -0.95 V regarding the copper-copper sulphate reference electrode.
- g. *Use of biocides* (see Sect. 2, 5.4 and 7.5).

Some microorganisms and substances of their secretion inhibit corrosion of metals. In conclusion, we have to emphasize, that if we determined that a system is severely deteriorated by microorganisms, none of the above-mentioned methods can prevent and decrease MIC. For example, if severe biofouling (several centimeters of thickness) is determined on the bottom of the fuel storage tank, or inside of fuel pipeline, only mechanical cleaning may help in such cases.

Table 5.8 Quality specification for methanol^a

Substance or property	Permitted Value, ppm max
Ethanol	50
Acetone	30
Water	1,000
Chlorides (as Cl ⁻)	0.5
Sulphur	0.5
Acidity (as acetic acid)	30
Total iron	0.1

^aIMPCA Methanol Reference Specification, International Methanol Producers & Consumers Association, Brussels, Belgium, 04 October, 2012, p 15

5.5 Corrosion in Biofuels

“Through measuring to knowing”

Heike Kamerlingh Onnes (1853–1926), a Dutch physicist.

Biofuels (alcohols and biodiesel) are organic solvents. Specialists who begin their using as fuels encounter the problems of materials' resistance to alcohols and esters (biodiesel). The problem of corrosion of metals in biofuels becomes acute because of their intensive growing use (see Sect. 4). We should mention that corrosion resistance can only be defined relatively to a metal and to a particular environment and conditions; it is not an absolute property. We will describe separately corrosion of metals in alcohols used as fuels and in biodiesel (esters). Methanol can contain contaminants such as ethanol, acetone, water, acids, chlorides, sulphur, and iron (Table 5.8).

Fuel grade ethanol (FGE) can contain contaminants such as methanol, butanol, acetone, organic acids, aldehydes, and ethers. These contaminants in FGE are specified by standards (Table 5.9).

Quality and contaminants in biodiesel also are specified by standards (Table 5.10).

In order to understand the behavior of materials in contact with alcohols and esters, we will describe physico-chemical properties of alcohols and esters using as fuels.

5.5.1 Physico-Chemical Properties of Biofuels.

Three general categories of organic liquids exist: *polar protic liquids*, *nonpolar aprotic liquids*, and *polar aprotic liquids*.

Polar protic liquids are those that can provide protons (H⁺) to other molecules or take away protons from other molecules. The examples of protic liquids are carboxylic acids (RCOOH), amines (RNH₂), amides (RCONHR₁), and in less extent *alcohols* (ROH). They are generally miscible with water (another polar protic liquid, H₂O) and can dissolve both organic and inorganic compounds. This property is very important for understanding corrosiveness of alcohols to metals and aggressiveness to polymers.

Table 5.9 Quality specification for FGE per different standards

Substance or property	Units	Permitted Value			
		ASTM D4806 (USA)	Brazil ^a	India ^a (IS 15464–2004)	EN 15376 (Europe)
Ethanol	% vol, min	92.1	99.3	99.5	96.7
Methanol	% vol, max	0.5		0.038	1
Water	% vol, max	1.0	~0.4		0.3
Denaturant ^b	% vol	1.96–4.76			
Acidity (as acetic acid)	mg/l, max	56	30	30	56
Chlorides	mg/l, max	8			20
Phosphorous	mg/l, max				0.5
Sulphur	ppm, max	30			10
Sulphate	ppm, max	4			
Copper	ppm, max	0.1	0.07	0.1	0.1

^aAnhydrous ethanol^bThe USA is unique in requiring the addition of a denaturant in order to render the ethanol undrinkable**Table 5.10** Quality specification for biodiesel per different standards

Substance or property	Units	Permitted value	
		ASTM D6751 (USA)	EN 14214 (Europe)
FAME ^a	% mass, min		96.5
Density at 15 °C	kg/m ³		860–900
Methanol	% mass, max	0.2	0.2
Water	% mass, max	0.05	0.05
Glycerin (total)	% mass, max	0.24	0.25
Acid number	mg KOH/g, max	0.5	0.5
Sulphur	ppm, max	15 (S15 grade ^b) 500 (S500 grade ^b)	10
Phosphorous	ppm, max	10	4
Copper strip corrosion ^c	Color rating, max	No. 3	No. 1

^aFatty acid methyl esters, produced from vegetable oils, i.e., rapeseed, palm, soy, sunflower oil^bASTM 6751 has two grades: S15 and S500. Almost all biodiesel is already S15^cThe copper strip corrosion gives an indication of the presence of certain corrosive substances (such as sulphur or acidic compounds) which may corrode equipment. This test assesses the relative degree of corrosivity of a petroleum product [7]

Nonpolar aprotic liquids are those in which protons do not dissociate. They are, for instance, aliphatic and aromatic hydrocarbons (RH, ArH; see Appendix A)—main components of petroleum products and fuels; they are immiscible with water and are very poorly dissolve alcohols. The shorter the length of hydrocarbon radical R (less number of carbon atoms in alcohol), the lower mutual dissolution of hydrocarbon and alcohol. Therefore there is a problem when alcohols are mixed with conventional fuels because they cannot form homogeneous solutions and at last are separated into two different phases after some period of mixing and storage.

The third group of organic liquids are *polar aprotic liquids*, namely, *esters* (RCOOR_1), ketones (RCOR_1), ethers (ROR_1), and aldehydes (RCOH). *Esters* are the base of biodiesel (see Sect. 4). The protic or aprotic character of pure solvents is a vital factor for corrosion. The existence of one-phase or multiphase liquid state is crucial. The resistivity of metals in organic solvents is influenced by the type and structure of the organic compound.

Corrosion of metals in organic liquids (biofuels among them) is not fundamentally different from corrosion of metals in aqueous solutions. Therefore similar variables (dissolved water and oxygen, acids, bases, ions, microorganisms, temperature, fluid regime and velocity) can affect corrosion both in organic and aqueous solutions.

5.5.2 Corrosion of Metals in Alcohols

We showed that corrosion mechanism in nonpolar aprotic liquids (petroleum products) is electrochemical owing to participation of dissolved water and oxygen (see Sect. 5.3). Probably, dissolved oxygen in alcohols plays also the same role of cathodic depolarizer. The solubility of oxygen is nearly ten times higher in alcohols than in water but less than in hydrocarbons (see Appendix E). The cathodic reduction of oxygen in the presence of ethanol (and presumably methanol) has also been proposed as follows [8]:



The electrical conductivity of alcohols is usually less than that of pure water but significantly more than that of petroleum products (see Appendix G). Electrode potentials of various metals in water, methanol and ethanol are nearly similar (the same order) while electrode potentials are not formed on metals in contact with petroleum products because they are not electrolytes. Therefore we can expect that corrosion processes and galvanic interactions would be similar in water, methanol and ethanol.

Three factors are needed for occurring galvanic corrosion: two different metals, physical (electrical) contact, and general electrolyte (see Sect. 5.2). Galvanic corrosion is not observed in gasoline which does not contain alcohols (for instance, in pure gasoline) or containing ethers (e.g., MTBE). This is because addition of ethers to gasoline does not increase the solubility of water and therefore the conductivity of the hydrocarbon phase. Whenever water is present in blends gasoline/alcohol, the electrical conductivity of the blend solution increases to the extent that galvanic corrosion is enabled. An example of this resulted in a methanol tank fire when the aluminum alloy flame arrester corroded to the point of being non-functional.

Solubility of water and oxygen in biofuels is very important because they are responsible for corrosion to occur in biofuels. Water and oxygen may be present at small concentrations in biofuels, but have dramatic effect on corrosion of metals. Alcohols have high tendency to absorb water from the atmosphere. For instance, 100 ml of methanol exposed to laboratory air at 25 °C with a relative humidity of 55%, in-

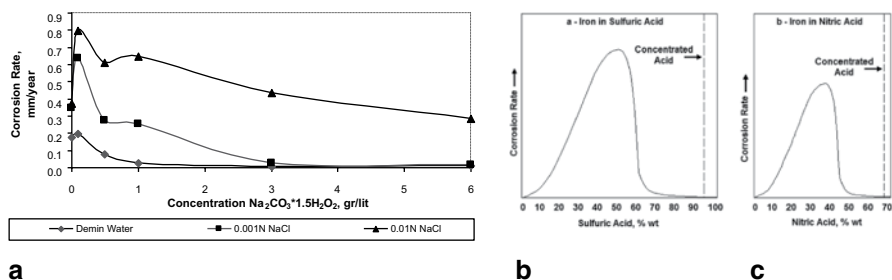


Fig. 5.22 **a** Corrosion rate of mild steel in different solutions of NaCl versus concentrations of sodium peroxocarbonate ($\text{Na}_2\text{CO}_3 \cdot 1.5\text{H}_2\text{O}_2$). **b** and **c** Effect of sulfuric and nitric acids on the corrosion rate of iron. [1]

creases water content from 350 ppm to 4,200 ppm (12 times fold!) in 2 h. Water content in ethanol is also increased after its exposure to atmosphere. These facts illustrate that tanks containing alcohol fuels must be carefully isolated from the atmosphere.

The lower amount of carbon atoms in alcohol, the greater amount of water can dissolve in it and this alcohol is more corrosive to metals. The first three alcohols (methanol, ethanol, and propanols) are completely miscible with water. The solubility of water in butanol is lower and equals to ~ 10 wt%. For comparison, the solubility of water in gasoline is < 0.01 wt%.

Small concentrations of water in alcohols can accelerate corrosion of metals. However, larger concentrations of water (> 0.1 wt%) in alcohols can passivate surface of some metals. This situation is common in corrosion. For instance, small concentrations of dissolved oxygen, peroxides, nitric and sulphuric acids in water accelerate corrosion of iron. However, their large concentrations passivate iron (Fig. 5.22).

Concentrations of water for passivation of metal surface depend on the type of a metal and an organic solution. For instance, aluminum is passivated when 1 wt% H_2O is added to methanol and ethanol at their boiling points. A threshold minimum concentration of water of about 0.25 wt% is required to suppress the corrosion of magnesium by gasoline/methanol blends. Iron, nickel, and stainless steel become passive when 0.1–1 wt% water is added to acidified methanol. Gasoline/alcohol blends containing large amounts of water may introduce new degradation mechanisms for materials. Close to the water content required for passivation of metallic surface, aqueous phase separation occurs (see Sect. 3). Considerable loss of lubricity, leading to increased wear of wetted parts, is also observed near the point of phase separation. Corrosion and wear products may become entrained in the fuel and cause subsequent drive ability problems in vehicles.

Dissolved oxygen plays similar role in corrosion of carbon steel in FGE, namely, dissolved oxygen in large concentrations can passivate carbon steel in ethanol (Table 5.11).

Pure methanol is non-corrosive to most metals at ambient temperatures; exceptions include magnesium and lead. Corrosion rates of carbon steel (UNS G10200), gray cast iron (CL 30), aluminum alloy (Al5052-H32) and stainless steel (UNS S30400) in M15 are very-very low: 0–0.5 $\mu\text{m}/\text{year}$ after 6 months of exposure at 25 $^\circ\text{C}$.

Table 5.11 Corrosion rates of carbon steel in FGE as a function of oxygen concentration in the purging gas. [9]

Concentration of oxygen concentration in the purging gas, % vol	0	1	5	21
Corrosion rate of carbon steel, $\mu\text{m}/\text{year}$	13.5	1.7	0.1	0.04

Methanol can be oxidized on metallic surface with formation of corrosive formic acid (HCOOH), especially at high temperatures.

Data about corrosion of some metals and alloys in alcohols and alcohol blended fuels are shown in Tables 5.12–5.15.

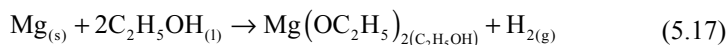
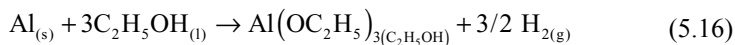
Corrosion rate of carbon steel in mixtures CH_3OH + Fuel C (50% iso-octane + 50% toluene) + H_2O of various compositions showed less than $2.5 \mu\text{m}/\text{year}$ [10]. Carbon steel and stainless steel are resistant to pure ethanol and its mixtures with water at 20°C (see Table 5.13).

If contaminants are present in ethanol, general and pitting corrosion of carbon steel occur (see Table 5.14).

If different contaminants (water, chlorides, sulphur-containing compounds, etc.) are present in methanol and ethanol, general and different types of localized corrosion of metals and alloys occur (see Table 5.15).

Carbon steel, cast iron, aluminum, and zinc are prone to general corrosion, sometimes pitting corrosion, both in methanol and ethanol, mostly in the presence of chlorides and small concentration of water. Titanium is prone to stress corrosion cracking and hydrogen embrittlement in methanol, and severe general corrosion in mixtures of ethanol and 20% HCl . Aluminum and its alloys are susceptible to general corrosion in mixtures of ethanol + isooctane + benzene at 130°C . Pitting corrosion develops on the surface of the aluminum alloy A384 after 24 h of the immersion in E10, E15 and E20 at 100°C . The number and dimensions of the pits increases with increasing ethanol content. No corrosion damage is observed below 100°C [13].

Aluminum is not resistant to ethanol, propanol, and butanol at elevated temperatures. Aluminum and magnesium can corrode in ethanol according to the reactions:



Aluminum alcoholate (alkoxide) dissolved in ethanol does not protect aluminum surface and aluminum is attacked continuously. The Russian chemist Alexander Tishchenko observed corrosion of aluminum in isopropanol in 1898:

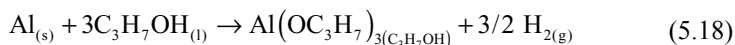


Table 5.12 Corrosion rates ($\mu\text{m}/\text{year}$) of metals/alloys in methanol-gasoline blends^a

Metal/alloy ^b	M85	M15
		(Aqueous phase)
SS 304	0	0
SS 444	0.1	0
Tin	0.2	0.5
Carbon steel	1.8	7.6
Brass	6.4	6.7
Zinc-Iron	7.5	13.3
Zinc-Nickel	13.3	11.9
Zinc	13.9	2.1
Zinc-Cobalt	18.1	9.0
Cadmium	22.9	35.7
Aluminum 356	24.0	
Aluminum 319	55.0	
Aluminum 380	63.0	
Terne plate ^c	86.9	12.9
Magnesium	146380.0	

Metals and alloys were immersed in methanol-gasoline blends at 40 °C for 2000–8000 h

^aLash RJ (1993) The corrosion behavior of metals, plated metals, and metal coatings in methanol/gasoline fuel mixtures, SAE Technical Paper Series no. 932341

^bChemical composition of alloys is given in Appendix H

^cTerne plate is an alloy coating that was historically made of lead (80 wt%) and tin (20 wt%) used to cover steel. Nowadays lead is replaced with zinc (50 wt%)

Table 5.13 Corrosion rates of carbon steel and stainless steel in pure ethanol and its mixtures with water^a. [11]

Water content in ethanol, mass %	Corrosion rate, $\mu\text{m}/\text{year}$	
	Carbon steel ^b	Stainless steel ^c
0	2.2	0
10	3.1	0.005
30	—	0.146
50	—	0.257

^aImmersion period lasted 3,000 h at 20 °C

^bCarbon steel St3 (designation in Russia)—equivalent to UNS G 10300

^cStainless steel X18N10T (designation in Russia)—equivalent to UNS S32100

Table 5.14 Corrosion of carbon steel in pure ethanol and Brazilian FGE. [12]

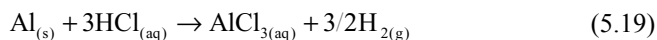
Medium	Corrosion Rate, $\mu\text{m}/\text{year}$	Corrosion Form
Pure Ethanol	0.15–0.25	General
Fuel Grade Ethanol	2.5–47.5	Pitting, General

Table 5.15 Corrosion of some metals and alloys in alcohols and alcohol blended fuels

Fuel	Contaminants in fuel	Metal/Alloy	Type of corrosion attack	T °C	Prevention of corrosion
Methanol	Methyl formiate	Carbon steel, Zinc	General corrosion	20–25	Elimination of methyl formiate
	<0.05 % H ₂ O	Aluminum	General corrosion, pitting	BP (64.7 °C)	Add 1 % H ₂ O
	Chlorides	Titanium	SCC, HE	20–25	Elimination of chlorides and add H ₂ O
Ethanol	Chlorides	Carbon steel, Cast iron	General corrosion, pitting	20- BP (78 °C)	Elimination of chlorides, deaeration
	<0.05 % H ₂ O 20 % HCl	Aluminum Titanium	Pitting General corrosion: 5 mm/y	BP (78 °C) 20–25	Add 1 % H ₂ O Add 9–30 % H ₂ O
45 % isooctane + 45 % benzene + 10 % ethanol		Aluminum, Aluminum alloy AlSi9Cu3	General corrosion	130	Add H ₂ O: 0.125 % for Al and 0.0625 % for AlSi9Cu3
40 % isooctane + 40 % benzene + 20 % ethanol		Aluminum, Aluminum alloy AlSi9Cu3	General corrosion	130	Add H ₂ O: 0.350 % for Al and 0.125 % for AlSi9Cu3
7.5 % isooctane + 7.5 % benzene + 85 % ethanol		Aluminum, Aluminum alloy AlSi9Cu3	General corrosion	120	Add H ₂ O: 0.350 % for Al and 0.250 % for AlSi9Cu3

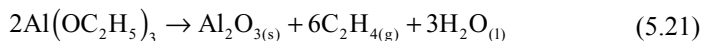
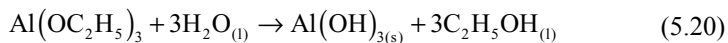
BP Boiling Point, *SCC* Stress Corrosion Cracking, *HE* Hydrogen Embrittlement

Thus alcohols behave as acidic solutions. We may compare the reactions (5.16 and 5.18) with the reaction of aluminum with aqueous solution of hydrochloric acid:



Reactions (5.16, 5.18 and 5.19) are related to pure aluminum surface. Usually aluminum contacting air is covered by tenacious and very dense film Al₂O₃ which prevents the metal from further oxidation. Therefore the surface of aluminum is opaque (inherent to Al₂O₃) and not shiny. Aqueous solution of hydrochloric acid dissolves aluminum oxide film Al₂O₃. Ethanol and isopropanol do not dissolve this film at ambient temperatures, however, can dissolve at high temperatures. Alumi-

num alcoholate formed in reaction (5.16) can be hydrolyzed according to (5.20) or decomposed according to (5.21).



Loose white-colored unprotected aluminum hydroxide $\text{Al}(\text{OH})_{3(s)}$ is formed in (5.20) and protective aluminum oxide $\text{Al}_2\text{O}_{3(s)}$ is formed in (5.21). Sometimes dissolution of aluminum in dry alcohols (5.16) is called *dry corrosion*. Water is produced according to reaction (5.21), hydrated alcohol will be formed and blends gasoline/alcohol can not remain dry when in contact with aluminum and magnesium.

Methanol and water form a homogeneous mixture which can separate from gasoline under certain conditions. Addition of methanol to gasoline increases substantially the temperature at which phase separation occurs. This problem is exacerbated because the aqueous phase is denser than gasoline, and thus sinks to the bottom of the tank where it then is transferred into the fueling system. This aqueous solution of methanol as separate phase can potentially be more corrosive to some metals, and more aggressive to some polymeric materials. Besides containing water, the bottoms phase will also contain some aromatics from the gasoline blend which also more aggressive to most polymers (see Sect. 6).

The use of co-solvent alcohols (ethanol, isopropanol, n-butanol, and tertiary butanol) is needed in colder weather in order to provide better solubility of methanol in gasoline and low temperature phase stability. Butanols are about 50% more effective than ethanol for adding water tolerance to the M10 which means that about 50% more ethanol will need to be used to achieve a targeted water tolerance as compared to using a butanol as co-solvent.

If the methanol-water mixture is formed within a gasoline-methanol blend and separates from the gasoline as separate phase, then localized corrosion may be accelerated. Corrosion of metals components in the equipment does not appear to be of consequence unless phase separation has occurred. If the water phase accumulates chlorides due to proximity to a coastal environment, then various localized corrosion phenomena (including chloride stress corrosion cracking of high carbon and austenitic stainless steel weld heat-affected zones) may occur. Therefore methanol-gasoline blends include co-solvents and corrosion inhibitors.

In general, a material which is resistant to methanol will be at least equally resistant to ethanol. Minimizing water in alcohol fuel systems is one way of reducing corrosion problems. However, magnesium and magnesium alloys corrode very rapidly in dry methanol and ethanol (see reaction 5.17 and Table 5.12).

Alcohols loosen rust and dirt from the fuel tanks and pipelines walls. Therefore these fuel systems need more frequent cleaning and inspection. Fuel systems which have been used in former gasoline service should be completely cleaned out before use of alcohol blended fuels. Fuel storage in tanks or vehicles must be pro-

tected from water absorption. This reaches by storing of methanol, ethanol and their blends with gasoline in a fixed roof tank with an internal floating roof. Nitrogen blanketing of the tank headspace will also provide additional protection against any penetrated moisture (see Sect. 7.6). Thus dehumidification of air in contact with methanol and ethanol is needed during its storage and transportation.

Corrosion inhibitors are recommended in concentrations 50–150 ppm for prevention general corrosion of carbon steel in contact with ethanol and its blends with gasoline. The selection of the proper inhibitor must be done carefully because the selected inhibitor may emulsify and/or foam. Effective inhibitors are mono-, di-, tri- ethanolamines and other amines. The commonly used passivation compound is a class of polyalkaline polyamines, e.g., 5 % solution of tetraethylenepentamine.

Carbon steel is susceptible to stress corrosion cracking (SCC) in fuel methanol and ethanol under particular conditions. The causes and prevention SCC of carbon steel in fuel methanol and ethanol will be described below.

5.5.2.1 Stress Corrosion Cracking of Carbon Steel in Methanol and Ethanol

Metals and alloys subjected to constant tensile stresses and exposed to certain environmental conditions (type, concentration of aggressive compounds and temperature) within certain electrode potential range may develop cracks, and this phenomenon is called *stress corrosion cracking* (SCC). The result is fracture caused by combination of mechanical loading and chemical attack. Not all environments and concentrations of aggressive compounds can cause SCC, but sometimes even pure water may induce SCC of some alloys.

Only two alcohols, methanol and ethanol, cause SCC of carbon steel. Probably the first description of SCC of carbon steel in methanol was made by K. Matsukura, et al., in 1976 [14]. Methanol containing chlorides can cause SCC of titanium (see Table 5.15). Methanol containing 0.05–0.5 % vol. water and dissolved oxygen at 20 °C or 0.005–0.04 wt% formic acid at 60 °C also can cause SCC of carbon steel. The absence of dissolved oxygen in methanol decreases the potential of SCC.

Ethanol as a fuel has been used since the nineteenth century. However, SCC of carbon steel storage tanks and pipes containing fuel ethanol was detected in 1980–1990s. Tens incidences of SCC failures in fuel ethanol storage tanks at blending terminals, associated piping, and fittings were detected in different regions in the USA.

The factors leading to SCC of carbon steel in fuel ethanol are dissolved oxygen (the main reason), the presence of chlorides (even less than 5 ppm) and methanol in ethanol and its blends with gasoline, and existence of scale and rust on carbon steel surface. Dissolved oxygen at concentrations above 10 ppm can cause SCC of carbon steel in fuel ethanol. Solubility of oxygen in ethanol is ~86 ppm (see Appendix E, Table E.4). Thus elimination of these factors can prevent SCC of carbon steel in ethanol.

The metallurgical type of carbon steel plays no significant role in promoting SCC. SCC of carbon steel does not occur when the ethanol content in ethanol-gaso-

line blends is less than 10% vol. If the ethanol content above 10% vol., SCC of carbon steel may occur if the oxygen content in the air space is above about 0.2% vol. In order to prevent SCC of carbon steel in all ethanol-gasoline blends concentration of dissolved oxygen must be below 8 ppm (10 times less than solubility value).

Ethanol containing small additions of LiCl and H_2SO_4 also can cause SCC of carbon steel. Additions of 0.01% acetic acid and 0.1% water to ethanol also can cause SCC of carbon steel but less severe than found in methanol. Additions of 0.10–25% formic acid and 0.1% water, 5% methanol or mixture of 5% methanol and 0.5% water to ethanol do not cause SCC of carbon steel.

Acid-producing ethanol-eating bacteria *Acetobacter aceti* increase crack growth rates of pipeline carbon steel 25-fold compared to what would in air [15].

Alcohols themselves are not known to have any particular aggressive effect on iron, so a reasonable hypothesis is that the alcohol is being oxidized in the cracks to formic acid (HCOOH), acetic acid (CH_3COOH), and carbon monoxide (CO) that cause SCC.

The experience of use of fuel ethanol in industry shows paradoxical results regarding SCC of carbon steel. User's storage and transportation equipment (bottom plates of tanks, pipes, roof hanger springs and air eliminators) exposed to fuel ethanol were subjected to SCC in the USA. This occurred with fuel ethanol which did not contain denaturants and inhibitors. However, SCC did not occur in manufacturing facilities (fuel ethanol producers), transportation trucks, rail cars, and service stations in the USA. Brazil, the first country which has produced and distributed fuel ethanol since 1970s, has also not reported any SCC of equipment for storage and transportation of fuel ethanol.

Cyclic loading such as that induced by emptying and refilling a large tank can cause fresh plastic deformation at the tips of pre-existing flaws, which can cause SCC. When carbon steel is exposed to E95, crack growth occurs initially. Even when the ethanol content is reduced to 20% vol. (E20), cracking does not stop completely. However, the crack growth stops when the ethanol content is reduced to 10% vol. (E10). Thus SCC of carbon steel will not occur in ethanol-gasoline blends below 10% vol. of ethanol, even if inhibitor is absent. Cracking can restart if ethanol is increased to 95% vol. (E95). If an inhibitor is added, cracking slows down and when oxygen is removed by purging the ethanol with nitrogen, cracking stops. Thus following preventive measures of SCC of carbon steel in ethanol can be used.

- a. Deaeration (removing oxygen) to concentrations lower than 8 ppm in fuel (independent of the ethanol and gasoline blending ratios). Deaeration can be carried out by injection of scavengers (e.g., ascorbic acid) or purging of inert gas (e.g., nitrogen or argon), vacuum treatment, and reacting with steel wool. Deaeration of small volumes of ethanol may be viable option to mitigate SCC. However, deaeration of large volumes of ethanol is not time and cost effective.
- b. Corrosion inhibitors (e.g., ammonia, diethanolamine) are recommended for mitigation SCC of carbon steel in ethanol and their blends with gasoline.

It is difficult to detect SCC, especially at its early stages, by standard inspection tools.

The probability of leakage is a complex function of SCC growth rate, which itself is a function of cyclic stress intensity, dissolved oxygen concentration, inhibitor type and its concentration, and ethanol content in blends.

SCC of tanks and pipes containing ethanol can result in leakage which in its turn to fire and environmental damage. The only foams recommended for ethanol fire suppression are the AR-AFFF (Alcohol-Resistant Aqueous Film-Forming Foam) and AR-FFFP (Alcohol-Resistant Film-Forming Fluoroprotein) foams. Environmental damage occurs because ethanol is good solvent and when penetrating into soil and groundwater can dissolve different organic constituents which are already present. For instance, ethanol acting as an oxygen absorber can inhibit degradation of benzene in the soil. Ethanol can degrade due to bacterial action to form methane.

Material Compatibility with Alcohols Methanol and ethanol tanks are constructed of either carbon steel or stainless steel (usually UNS S30400). Material compatibility with gasoline-alcohol blends are shown in Table 5.16. Not recommended metals and alloys are shown in Table 5.17.

Guidelines for designing, fabricating, constructing, repairing, and safeguarding aboveground biofuel storage tanks is essentially the same as that for conventional liquid fuels such as gasoline, and flammable organic solvents such as benzene, toluene, and acetone [19, 20]. However, physico-chemical properties of alcohols are unique and are not the same as those of other liquid fuels. Possible corrosion is very important problem. For instance, water on bottoms may have a higher concentration of alcohols than the gasoline-alcohol blend, and therefore may be more damaging or aggressive to internally lined (by organic coatings) tanks and cause corrosion. Galvanized steel is not suitable for methanol service.

Methanol may cause SCC of titanium alloys. SCC failures occurred in dry methanol, methanol-acid and methanol-halide (containing chlorides, bromides or fluorides) solutions. Water is an effective inhibitor of SCC and maintains the passivity of titanium alloys in some environments. Whereas, SCC has been observed in ethanol tanks made from carbon steel, this phenomenon has not been reported for methanol tanks.

Some older internally lined (examined previously only in contact with gasoline) steel tanks may not be suitable for contact with gasoline-alcohol blends. Methanol is more aggressive to organic coatings than hydrocarbons containing in gasoline. Many tank liners (organic coatings) installed in the past can be damaged by these blends.

Before the use of fiberglass-reinforced tanks for the storage of gasoline-methanol/co-solvent blends they must be examined for compatibility under particular conditions because some resins in the fiberglass-reinforced matrices are not resistant to gasoline-methanol/co-solvent blends.

Cathodic protection can be used with impressed current. Sacrificial anodes are unacceptable because during dissolution they increase contaminants in the fuel alcohols. Contaminants may be soluble and insoluble. Soluble contaminants, such as chloride ions, increase the electrical conductivity of the fuel alcohols and attack passivating oxide films on several metals and alloys causing pitting corrosion.

Table 5.16 Recommended Materials in Gasoline-Alcohol Blends^a. [16–18]

Alcohol	Recommended metals/alloys
Methanol, Ethanol	Carbon steel
	Stainless steel
	Bronze
Methanol	Aluminum
Ethanol	Tin
	Iron-cobalt alloy
	Nickel plate
	Pre-painted zinc-nickel

^aGasoline-Methanol blends contain co-solvents (ethanol, propanols, or butanols)

Table 5.17 Not Recommended Materials in Gasoline-Alcohol Blends^a. [16–18]

Alcohol	Not Recommended Metals/Alloys
Methanol	Galvanised steel
Ethanol	Magnesium
	Aluminum
	Zinc and zinc alloys
	Cast iron
	Copper
	Brass
	Terne ^b coatings
	Galvanic contacts SS and Al6061 or Al319; cast iron and Al6061 or Al319 ^c

^aGasoline-Methanol blends contain co-solvents (ethanol, propanols, or butanols)

^bTerne is an alloy coating made from lead (80 wt%) and tin (20 wt%) used to cover steel

^cChemical content of alloys is given in Appendix H

Increased electrical conductivity promotes corrosion currents on metallic surface. Insoluble contaminants usually are corrosion products (e.g., aluminum and ferric hydroxides) which clogs the fuel systems over time. To prevent corrosion the fuel systems must be made of suitable materials, fuel alcohols should have a low concentration of contaminants and have a suitable corrosion inhibitor added.

5.5.3 Corrosion of Metals in Biodiesel

Biodiesel is an ester (FAME or FAEE—see Sect. 4). One of the most important impurities in biodiesel is water. The water content in biodiesel may increase with storage period. The presence of water in biodiesel can enhance hydrolysis of esters, resulting in the deterioration of the biodiesel characteristics. Water may appear in biodiesel because it is hygroscopic, or as a residual water left from prior hydrotesting of fuel system. Similar to conventional fuels, water can be present in an emul-

sion with biodiesel or as a separate phase overlain by a biodiesel layer. In the latter case, the corrosivity of the aqueous phase depends on the chemical compounds diffusing from the biodiesel phase. Biodiesel can hold many times more dissolved water than conventional diesel fuel. Therefore biodiesel is not quite as soluble in ultra low sulphur diesel fuel because of the makeup of the fuel, so at lower temperatures it tends to separate. Free water is very difficult to remove from biodiesel using normal filtration means. The presence of water in biodiesel may induce the proliferation of microorganisms and increase corrosivity of biodiesel.

The experimental data of study of corrosion rates of carbon steel, aluminum, copper, brass and stainless steel in biodiesels produced from different oil and fat feed stocks and blends with conventional diesel fuels are shown in Tables 5.18–5.21. The data are analysed below.

Corrosion rates of carbon steel in biodiesel (soybean oil and animal fat based) and its blends with conventional diesel fuels (up to 0.4 wt% = 4,000 ppm sulphur) up to 1 vol% water usually range between 0.01 and 0.03 mm/year but do not exceed 0.09 mm/year (Table 5.18).

The data in Table 5.18 show that corrosion rate of carbon steel in B100 and its blends is low (0.01–0.03 mm/year). Therefore carbon steel can be used as construction material in contact with biodiesel. Addition of 5% of aqueous solution containing 0.006% acetic acid to biodiesel increases corrosion rate of carbon steel to 0.14 mm/year (10 times more than in pure biodiesel). Shallow pits of 13 μm deep are formed on the surface of carbon steel after 3 months of immersion in biodiesel containing 5% vol. of aqueous solution containing 0.006% of acetic acid.

It is interesting to emphasize that corrosion rate of inner surfaces of carbon steel shells of storage tanks containing conventional diesel fuel ranges from 0.001 to 0.022 mm/year (see Sect. 5.8). This means that corrosion rate of carbon steel are low and similar both in biodiesel and conventional diesel fuel.

According to requirements of standards [22, 23] to biodiesel, water content must not exceed 0.05% vol., sulphur not more than 0.05% wt. and total acid number not more than 0.8 mg KOH/g biodiesel. The presence of 1% H_2O in pure biodiesel and its blends did not influence corrosion rate of carbon steel. Significant increase of total acid number (2–7 folds) of blends after exposure of carbon steel specimen at 43°C during 3 months show degradation of the biodiesel and its blends with conventional diesel fuel (oxidation of esters and hydrocarbons containing in fuels). Thus, biodiesel does not appear to be more corrosive to carbon steel than conventional diesel fuel, as long as it has not degraded via oxidation to be acidic. Typically biodiesel usually contains antioxidant additives (see Sect. 4).

Corrosion rates of carbon steel in biodiesels based on different feed stocks are very small with maximum value of 19 μm /year in the B100 based on Pongamia oil (see Table 5.19). Corrosion rates of carbon steel in B100 based on castor oil, soybean oil, used vegetable oil, and bovine fat even less: 0–0.08 μm /year (see Table 5.19). Corrosion rates of aluminum, copper and brass in biodiesel are also very low.

It is important to explain small corrosion rates of metals in biodiesel. The presence of free water or emulsion water-in-oil in biodiesel does not necessary lead to corrosion of metals. Competition of adsorption of water and ester (biodiesel) mol-

Table 5.18 Corrosion rates of carbon steel in biodiesel B100 (soybean oil and animal fat based) and its blends (% vol.) with conventional diesel fuel. [21]

Biodiesel (based on) % vol.		Diesel Fuel ^a		Added water (1 % vol.)	TAN, mg KOH/g		Corrosion rate, mm/ year
Soybean oil	Animal fat	ULSD	4,000 ppm Sulphur ^b		Before immersion	After immersion	
100		0		No	0.37	2.77	0.014
50		50		No	0.09	0.15	0
20		80		No	0.05	0.00	0
5		95		No	0.01	1.82	0.003
0		100		No	0.00	0.10	0.013
100		0		Yes	0.37	0.56	0.018
50		50		Yes	0.09	0.00	0
20		80		Yes	0.05	2.27	0.080
5		95		Yes	0.01	0.94	0
0		100		Yes	0.00	0.04	0.010
	100	0		No	0.86	2.57	0.013
	50	50		No	0.43	2.50	0.016
	20	80		No	0.18	2.52	0.010
	5	95		No	0.09	0.47	0.005
	0	100		No	0.07	0.05	0.020
	100	0		Yes	0.86	2.50	0.010
	50	50		Yes	0.43	2.56	0.028
	20	80		Yes	0.18	2.55	0.013
	5	95		Yes	0.09	0.37	0.090
	0	100		Yes	0.07	0.04	0.028
	20		80	No	0.28	0.31	0.020
	5		95	No	0.18	0.19	0.028
	0		100	No	0.16	0.18	0.029
	20		80	Yes	0.28	0.46	0.026
	5		95	Yes	0.18	0.17	0.024
	0		100	Yes	0.16	0.15	0.030
95				5 % of aqueous solution con- taining 0.006 % acetic acid			0.14

Immersion of carbon steel specimen was at 43 °C for 3 months. TAN Total Acid Number, ULSD Ultra Low Sulphur Diesel (containing 7 ppm total sulphur)

^aDiesel fuel in % vol

^bDiesel fuel containing 4,000 ppm sulphur

Table 5.19 Corrosion rates of some metals and alloys in biodiesel and its blends with conventional diesel fuel

Media		Corrosion rate, $\mu\text{m}/\text{year}$					Reference
		Carbon steel	Aluminum	Copper	Brass	SS 316	
Conventional Diesel Fuel ^a		0.07	0.1	0.2	0.1	0.05	[24]
B5 and B20 (nonaged) ^b		0.1	0.1–0.3	0.5	0.2–0.7	0.05	
B5 and B20 (aged ^c)		0.4	0.5	0.7	0.3–0.6	–	[25] ^f
B100 ^d		19	56	26	10		
B99 ^e		96	73	19	8		
3 % NaCl aqueous solution		80	57	45	22		
Biodiesel (based on)	Bovine fat	0.03–0.07				0.04–0.09	[26] ^g
	Soybean oil	0.03–0.06				0.05–0.09	
	Castor oil	0.02–0.08				0.05–0.08	
Conventional Diesel Fuel ^h		0.16					[27] ⁱ
Biodiesel (based on)	Soybean oil	0.02					[28]
	Sunflower oil	0.01					
Conventional Diesel Fuel ^a		0.9					
B100 ^j		0					
Two-phase mixture fuel + water ^l (in aqueous phase) ^k	B100 + water ^k	172.5 ^m 680 ⁿ					
	DF ^l + water ^k	260 ⁿ					

Carbon steel (G 10200), copper (C11000), brass (C26800), aluminum (A91100), and stainless steel (S31600). Chemical content of these alloys is given in Appendix H

^aConventional diesel fuel (ULSD—ultra-low sulphur diesel) containing 10 ppm sulphur

^bSoybean biodiesel (B100) and ULSD were used for preparation of the biodiesel/diesel fuel blends B5 and B20. They contained 10 ppm sulphur

^cB5 and B20 were aged at 35 °C for 6 months

^dBiodiesel (B100) was produced from Pongamia oil (Honge oil)

^eB99 is 99% biodiesel containing 1% vol. of 3% aqueous solution NaCl

^fImmersion period of metallic specimen was 100 h at ambient temperature

^gImmersion period of metallic specimen was 6 months at 35 and 70 °C. Water content was 0.05%, 0.1% and 0.14% (vol)

^hConventional diesel fuel contained 870 ppm sulphur

ⁱImmersion period of metallic specimen was 115 days at 60 °C

^jThe biodiesel (B100) was obtained from fresh (unused) and used vegetable oil stock

^kDeionized water

^lDF = Conventional Diesel Fuel

^mWeight loss method. Corrosion rate in aqueous phase

ⁿElectrochemical technique (named also wire beam electrode technique) allowing the measurement of the corrosion current between anodic and cathodic sites in the array [29–31]. Corrosion rate in aqueous phase

Table 5.20 Corrosion (qualitative estimation) of carbon steel in mixtures of biodiesel and water. [26]

Biodiesel (or Diesel fuel ^a) + 10% vol. H ₂ O	Percent of the test carbon steel surface corroded
Diesel fuel ^a	70
Bovine fat (B100)	100
Soybean oil (B100)	100
Castor oil (B100)	25
Bovine fat + Soybean oil (1:1)	60
Bovine fat + Castor oil (1:1)	<0.1
Soybean oil + Castor oil (1:1)	0

Tests were carried out according to NACE standard [32]: Immersion period of metallic specimen was 3.5 h at 38 °C during agitation

^aDiesel fuel is conventional diesel fuel containing <50 ppm sulphur

ecules decides about corrosivity of media. The ester molecules of biodiesel preferentially wets metal surface and plays the role of corrosion inhibitor (adsorbed layer type) in the presence of water molecules.

The corrosion rates of carbon steel, aluminum, copper and brass in biodiesel (based on Pongamia oil) with addition of 1 % vol. of 3 % NaCl aqueous solution and in 3 % NaCl aqueous solution (for comparison) also are low (see Table 5.19). However, the electrical conductivities of biodiesel after experiments (100 h) increased by about one order of magnitude. This increase might either be due to the increased ionic content due to small corrosion of metals and alloys in biodiesel or due to the absorption of moisture by biodiesel, or both. In either case it would appear that the corrosivity of biodiesel might increase during long-term storage.

Corrosion rates do not depend on water content in the range 0.05–0.14 % vol. H₂O, temperature (35 and 70 °C) and aging time (120 days) of biodiesel [26].

When biodiesel is mixed with greater amount of water (10% vol.) it becomes corrosive to carbon steel (Table 5.20). Two types of biodiesels (based on bovine fat and soybean oil) mixed with water (10% vol.) are more corrosive than conventional diesel fuel (with 10% vol.). However, biodiesel based on castor oil with similar quantity of water inhibits corrosion of carbon steel. This fact shows that origin of biodiesel in this particular case plays important role in its corrosivity based on qualitative estimation. Aqueous phase after contact with biodiesel becomes more corrosive to carbon steel: pH=3–4 [28]. This is similar to extraction of corrosive compounds from gasoline (see Sect. 5.3) showing that biodiesel contains corrosive compounds and in the case of water contamination aqueous phase will become corrosive. The decrease in the pH is likely a result of degradation of the biodiesel in the presence of water and dissolved oxygen. The increase of acidity of the biodiesel and the presence of the water layer, however, does not necessary lead to the increase in the corrosivity of the biodiesel. Carbon steel in aqueous phase after contact with biodiesel intensively corrodes while does not corrode in biodiesel. Corrosion rate in aqueous phase after contact with biodiesel is greater than that in aqueous phase after contact with conventional diesel fuel.

Table 5.21 Pitting corrosion (mm/year) of carbon steel in mixture biodiesel–seawater in the presence of microorganisms. [33]

Location of metal sample in media	Pitting corrosion rate, mm/year	
	Key West	Persian Gulf
Biodiesel	0.21	0.46
Interface biodiesel–seawater	0.40	0.06
Seawater	0.12	0.18

Biodiesel is soybean based (FAME). Immersion of carbon steel (UNS G10200) specimen was during 60 days at 23 °C. *Seawater* was used from Key West (Florida, USA) and Persian Gulf (Bahrain)

Carbon steel in contact with biodiesel is prone to pitting corrosion in the presence of microorganisms (Table 5.21). Pitting corrosion rate on carbon steel surface in biodiesel even is higher than in seawater.

Biodiesel is poorly soluble in seawater (7 ppm at 17 °C), and is readily biodegraded by aerobic microorganisms (the half-life in seawater is less than 4 days). However, anaerobic conditions prevail whenever heterotrophic microbial respiration consumes dissolved oxygen at a rate that exceeds diffusion. Methyl esters in biodiesel can be quite easily hydrolyzed and converted to a variety of fatty acids also by anaerobic microorganisms. Biodiesel is far more amenable to biodegradation process than hydrocarbons (components of conventional fuels).

Sometimes the surface of copper and brass is darkened and stained after immersion in biodiesel. Content of dissolved copper in biodiesel detected by atomic absorption spectroscopy significantly increases. In addition, water content and acidity of biodiesel increase after immersion of copper and brass in it. As a result biodiesel becomes out of specification (standards). These facts point out degradation (increase of acidity) of biodiesel in the presence of copper ions, thus increasing corrosivity of biodiesel and in its turn result in further corrosion of copper and brass. Corrosion of copper and brass in biodiesel is autocatalytic process. Thus copper and its alloys are not recommended for use in contact with biodiesel. Carbon steel, aluminum and stainless steel are more resistant to biodiesel and can be used as construction materials for its storage and transportation.

Vapor phase Corrosion Inhibitors (VpCI) can be injected into biofuel (ethanol and biodiesel) and its blends for anti-corrosion protection of carbon steel [34].

5.5.3.1 Material Compatibility with Biodiesel

Most tanks designed to store conventional diesel fuel will store pure biodiesel with no problem. Acceptable materials of storage tanks, trucks and railcars include aluminum, carbon steel, stainless steel, certain polymers (fluorinated polyethylene and polypropylene, Teflon), and fiberglass. Some pipes, valves, fittings and regulators are made from copper, brass, bronze, zinc, and tin. These metals and alloys may accelerate the oxidation of biodiesel causing formation of sediments and therefore are not recommended for use in contact with biodiesel. Galvanized steel and terne

coated steel are not compatible with biodiesel at any blend concentrations. Organic acids can be formed in biodiesel as a result of its oxidation by dissolved oxygen during long-term storage. These acids can increase corrosivity of biodiesel.

These facts point out the necessity of careful selection of materials for systems containing biodiesel.

5.6 Corrosion in the Atmosphere

Aboveground and underground storage tanks, pipelines, other constructions and equipment containing fuels can contact the atmosphere, water, and soil. Inner surfaces of upper parts of AST and UST are exposed to mixtures of atmospheric gases and hydrocarbons. Outer surfaces of AST and inner surface of AST containing outer floating roofs are exposed to the atmosphere. Outer surfaces of UST, AST bottoms and pipelines are exposed to soil. Therefore we will discuss corrosion in atmosphere and soil.

Atmosphere is a homogeneous gaseous media containing N_2 (78%), O_2 (20.95%) and small amounts of inert gases, CO_2 , and H_2O . The additional components in atmosphere may be contaminations depending on climate and industrial activity. Contamination may be natural and anthropogenic. The first are salts ($NaCl$, $MgSO_4$) coming from the oceans, sand (SiO_2) from the deserts, mountains and hills, various gases and dust from the volcanoes. Anthropogenic contamination is defined by the industrial activity: producing energy, chemicals, movement of vehicles, etc. The result is the emissions of acid gases, dust, water vapor, and other aggressive contaminants for metals.

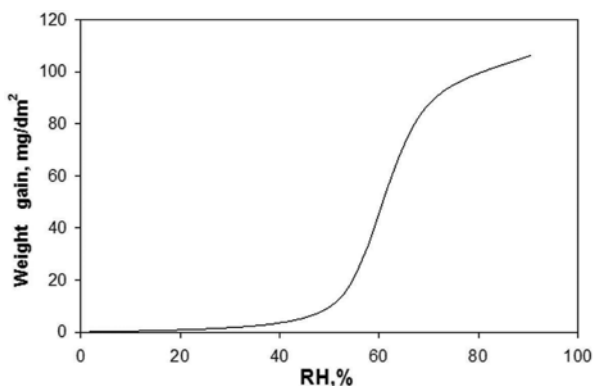
Nitrogen and inert gases do not influence corrosion of metals. Water vapors are always present in the air because of evaporative processes. *Relative humidity* (RH, %) is the ratio of actual water vapor concentration to saturated water vapor concentration in percent at a given temperature. For instance, if the actual water vapor concentration is 10 g/m^3 at 20°C and the saturation water vapor concentration is 17.3 g/m^3 at 20°C , the relative humidity is

$$RH, \% = \frac{10 \frac{\text{g}}{\text{m}^3}}{17.3 \frac{\text{g}}{\text{m}^3}} \cdot 100\% = 57.8\% \text{ at } 20^\circ\text{C} \quad (5.22)$$

Relative humidity depends on air temperature. The temperature, at which the moisture content in the air will saturate the air, is called the *dew point*. If the air is cooled, some of the moisture will condense.

The corrosion rate and lifetime of metallic constructions depend on the aggressiveness of the atmosphere, which is defined by climate and contaminations in the atmosphere. The climate is defined by nature and its factors are relative humidity, changes of temperature during the day–night cycle, the content and type of sediments, direction and the strength of winds. Following factors influence the corro-

Fig. 5.23 The influence of relative humidity (RH, %) on the corrosion rate (weight gain) of iron in air containing 0.01 % vol. SO_2 . [1]



siveness of the atmosphere: relative humidity, gases (SO_2 , SO_3 , NO_x , H_2S , CO_2 , NH_3 , etc.), salts (NaCl , MgSO_4), dust (particles of coal, sand, metals and their oxides), temperature and its changes, the value and period of the presence of a water layer on a metallic surface (time of wetness).

The relative humidity (to 50%) practically does not influence corrosion rate of iron in air containing $\sim 0.01\%$ vol. SO_2 (Fig. 5.23). The corrosion rate drastically increases at a relative humidity above 60% in the presence of acid gas SO_2 . This value is called the *critical relative humidity*. It is interesting to emphasize that such a critical value of water content was defined not only in the atmosphere, but also in gasoline, naphtha, and kerosene (see Sect. 5.3). This fact points out similar corrosion (electrochemical) mechanism in the atmosphere and in these petroleum products in thin layer of electrolytes with the participation of water and dissolved oxygen. The main cause of the formation of water layers on a metallic construction is the condensation of water on irregularities, in cracks and crevices on metal surface, in corrosion products, and on hard foreign particles (dust, salts, and soldering fluxes) on metal surfaces. Chloride and sulfate salts are the most aggressive corrosive agents. The number of layers of water on a metallic surface increases with an increase in relative humidity. Therefore, salt mist from the ocean, sea or chemical enterprises can significantly induce atmospheric corrosion.

Various gases influence differently corrosion of metals in the atmosphere. Carbon dioxide CO_2 , sulphur dioxide SO_2 and sulphur trioxide SO_3 (called also SO_x), nitrogen oxides N_xO_y (called also NO_x) are acidic gaseous. They dissolve in water droplets in the atmosphere forming carbonic acid H_2CO_3 , sulphurous H_2SO_3 , sulphuric H_2SO_4 and nitric acid HNO_3 which are aggressive to many metals and alloys: Fe, Zn, Ni, Cu, Al, and others, as well as to concrete.

Ammonia (NH_3) gas can be formed by reducing NO_x . Fertilizers may be also the source of ammonia in the atmosphere. It dissolves well in water droplets giving rise to alkaline solution. Ammonia gas and its solutions are corrosion inhibitors of carbon steels, however, are corrosive to copper, zinc, and their alloys, and may cause stress corrosion cracking of copper alloys.

Hydrogen sulphide (H_2S) is present in crude oils, natural hydrocarbon condensates, petroleum products, and sometimes is present in ground waters. Small concentrations of H_2S in the air cause tarnishing of silver and copper. This is the cause why silver and copper strips are used for qualitative determination of traces of hydrogen sulphide in fuels. Hydrogen sulphide in atmosphere may cause severe corrosion of silver and copper relay electric contacts.

Four types of atmospheric corrosion mechanisms are differentiated according to the time of wetness, and, as a result, to thickness of water layer on a metallic surface.

1. *Dry oxidation* occurs in the absence of water layer on the metal surface. This is a typical chemical mechanism, when oxidation of metals occurs by oxygen gas.
2. *Damp corrosion* occurs in the presence of a thin water layer which is impossible to observe it on a metal surface with the naked eye ($RH < 100\%$).
3. *Wet corrosion* occurs in the presence of water layer which is possible to observe on a metal surface with the naked eye ($RH = 100\%$).
4. *Sheltered corrosion* occurs inside of structures and equipment closed from the outer atmosphere when water vapors containing corrosive gases and salts are condensed on surfaces inside of metallic structures which do not dry for a long period. Inside surfaces of tanks are subjected to sheltered corrosion.

Methods of prevention and control of the atmospheric corrosion of tanks are described in Sect. 7.

5.7 Corrosion in Soil

Millions of kilometers of buried pipelines are used for the transportation of crude oil, fuels, natural gas, water, sewage, and many chemicals. Underground storage tanks containing fuels also are installed in soils. Sometimes AST bottoms contact soil. Many underground metallic structures and systems containing fuels are situated in high population regions, and any corrosion failure can result in a dramatic scenario for people and the environment.

If water and atmosphere are homogeneous phases, soil is a heterogeneous medium containing a mixture of solids, liquids and gases. In spite of this difference, metals corrode in soil according to an electrochemical mechanism with the simultaneous occurrence of anodic and cathodic reactions similar to that occurring in water and the atmosphere.

Soil is a three phase admixture of solid inorganic materials (coarse-grained rocks and minerals), solid organic matter (humus, plants, biological organisms and micro-organisms), liquid aqueous and organic solution, and gases. Large variations in soil components result in a wide range of corrosiveness of soils. Soil type, water content, permeability of air, position of the water table (upper level of an underground surface in which the soil permanently saturated with water), soil electric resistivity, soluble ion content, soil pH, oxidation-reduction (redox) potential, temperature, and

Table 5.22 Corrosiveness of soils in accordance with their electrical resistance

Electrical resistance of soil, Ohm·cm	Corrosiveness of soil
Below 500	Very corrosive
500–1,000	Corrosive
1,000–2,000	Moderately corrosive
2,000–10,000	Mildly corrosive
Above 10,000	Progressively less corrosive

presence of microorganisms are the main factors of soil corrosiveness. So many factors result in such situation that a unified theory describing all soil conditions that cause corrosion does not exist. Therefore, it has been suggested that corrosiveness of soils be classified qualitatively according to their electric resistivity or redox potential, but the former is more common (Table 5.22).

In any case, it will be useful to analyze all factors determining the corrosiveness of soils.

Soil type is determined by climate (arid, tropical, continental, arctic), and includes soil particle size distribution, structure, organic and mineral content. The soil particle size distribution and structure determine the physical properties and as a result the permeability of liquids and gases through soil. Pebbles, sand, silt and clay have different sizes of particles. The greater these sizes, the greater the permeability of water and gases through the soil. All this also influences the corrosion of metals in soils. For example, coarse-grained sands allow good drainage and easy access of atmospheric oxygen to underground metallic structures. Fine grained soils are more restrictive, but capillary forces can draw water up and keep soil water saturated even during relatively dry conditions.

The presence of water in soil (similar to fuels and atmosphere!) is a major factor for corrosion occurrence according to the electrochemical scenario. Three sources of water exist in soil: gravitational (rains and snow), groundwater (accumulation of gravitational water at the water table) and capillary water. Soil type also significantly influences the capacity of soil to maintain water and permeability for oxygen. Soil water content above 20% can be corrosive towards carbon steel and usually results in general corrosion (Fig. 5.24).

Water content less than 20% can result in pitting corrosion. Dry soils are not corrosive. Increase of soil moisture facilitates the anodic process, but impedes the cathodic process at high moisture content (aeration and diffusion of oxygen decrease), therefore the dependence of the corrosion rate of metals on water content in soil is described by a curve with a maximum (Fig. 5.25).

Permeability of air depends on water content and soil type (its density). The greater the permeability of soil, the more intensive the cathodic process, and as a result corrosion also increases. Non-uniform aeration of underground metallic surface results in the formation of differential aeration cells (Fig. 5.26): the cathodic process occurs on well aerated metal surfaces (sand) and the anodic process occurs on lower aerated metal surfaces (clay).



Fig. 5.24 Corroded underground pipes

Fig. 5.25 Influence of water content on corrosion of carbon steel 1 in sand and 2 in clay

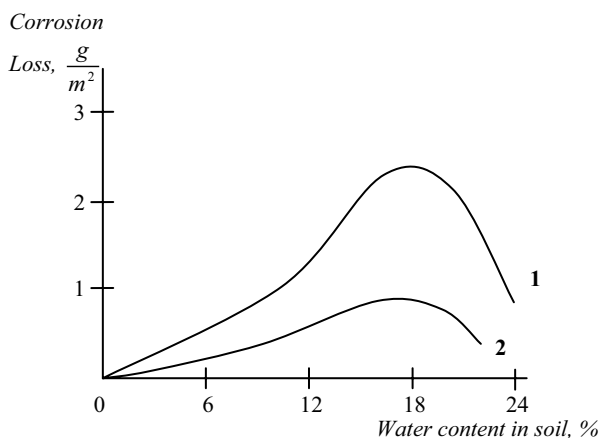
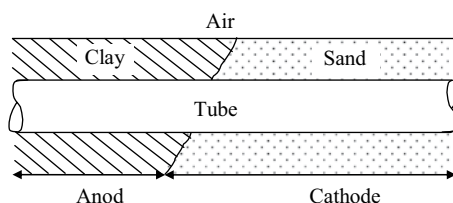


Fig. 5.26 Differential aeration cell appearance on the tube surface in soil with different permeability of air



Water table position is also important and can vary from 1 to 6 m depending on ground conditions, climate, and the season of the year.

Soil electric resistivity is defined by the ability to conduct electric current by means of ion migration, and depends on water content, type and amounts of electrolytes, and soil type (structure). Electric resistivity characterizes corrosiveness of soil for carbon steels and cast iron (see Table 5.22, excluding water saturated soils).

Mineral composition (salts and oxides) is an important factor of corrosion occurrence in soil. Clays (for example, kaolinite—aluminosilicate) are among the most common minerals on earth constituting nearly 30% of all sedimentary materials.

Sand (SiO_2) is relatively permeable, well drained and inert. Carbonates (limestone CaCO_3 or dolomite $\text{CaCO}_3 \cdot \text{MgCO}_3$) usually saturate groundwater and buffer the solution in the neutral to alkaline pH range. As a result of cathodic electrochemical reaction, natural or induced by cathodic protection, carbonate scale (calcite or dolomite) precipitates on the metal surface. Such scale forms an impermeable protective layer that indicates both effective cathodic protection and the near absence of corrosion. The presence of salts (e.g., chlorides, sulphates and nitrates) dissolved in water influences the electric resistivity of soils and as a result their corrosiveness. The greater the soil resistivity (less ion content), the less its corrosiveness and efficiency of cathodic protection.

The *pH* values of soils may range from 3.5 to 10, but most soils have neutral or near neutral pH (6–8). Soil can become acidic due to leaching of some salts (for example, CaCl_2 and $\text{Mg}(\text{NO}_3)_2$) by rainwater, and to dissolution of CO_2 in groundwater. Soils containing well-humified organic matter also tend to be acidic. Carbon steel corrodes intensively at $\text{pH} < 4$, but may be passivated at $\text{pH} > 9$. Amphoteric metals such as aluminum, zinc and their alloys are resistant in appropriate pH range: between 4.3 and 8.3 for aluminum, and between 6 and 12 for zinc. It is obvious that in neutral and slightly alkali soils the cathodic reaction on metal surfaces is a reduction of dissolved oxygen, and in acidic soils the cathodic reaction is a reduction of hydronium cations H_3O^+ .

Redox potential is defined by the presence of various oxidized states of the same element, for instance, O_2/OH^- , $\text{Fe}^{2+}/\text{Fe}^{3+}$, $\text{Mn}^{2+}/\text{Mn}^{4+}$. The first pair usually determines the redox potential of soil.

Microorganisms can significantly influence the corrosiveness of soil and cause MIC. SRB are the most widespread and important in soil corrosion. Anaerobic conditions existing in silt, mud, clay, and swampy soils are more likely to cause MIC. Aerobic acid-producing bacteria can also foster MIC. Burial of organic materials, water, sulphates, nitrates, ions Fe^{3+} and Mn^{4+} , and CO_2 , can promote bacterial activity and as a result MIC. Owing to the biological activity of soil organisms, oxygen concentration diminishes, but CO_2 amount increases to concentrations a hundred-fold higher than in the atmosphere. Sometimes organic coatings can foster microbial growth and activity causing MIC.

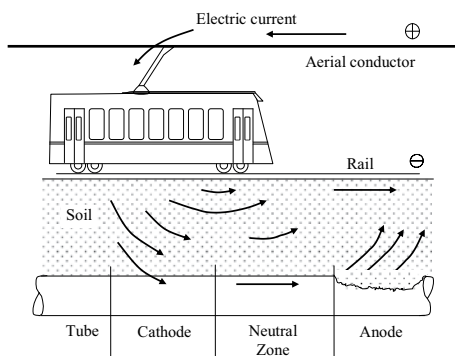
Spillage of organic solvents and fuels can also influence corrosiveness of soils and the protective properties of organic coatings. Heterogeneity of soil in structure, density, water and electrolyte content, and pH result in the formation of electrochemical heterogeneity and increasing non-uniform corrosion.

It is very important how metallic structures are installed in soil. They can be driven into the ground (piles), installed in excavations and then buried with backfill, usually sand (most pipelines), and inserted into predrilled shafts or horizontal tunnels (trenchless pipe installation).

Disturbed soil around the buried structures may also lead to a unique environment at the metallic surface. Such conditions can change access of atmospheric oxygen, foster biological activity and alter the chemical composition of aqueous phase contacting metallic structures.

Temperature of the earthen material at the depths of metallic constructions depending on geographical region, climate, season of the year and day-night cycle undergoes

Fig. 5.27 Scheme of appearance and mechanism of the activity of stray electric current



significant changes ranging between -50°C and $+50^{\circ}\text{C}$ (and even more), and as a result influences electrochemical kinetics and diffusion of aggressive components causing corrosion of underground metallic structures. The corrosion rate increases when soil thaws out, and decreases when soil freezes. All the above-mentioned factors define corrosion type and the corrosion rate of metallic structures in soil.

Corrosion by Stray Electric Current Electric installations (electric railways, trams, cathodic installations, electrolysis plants and galvanic baths, welding units, and electric ground connections of direct current) can produce *stray electric current* and cause severe corrosion of underground metal structures lying in the zone of these stray currents (Fig. 5.27).

Stray electric current (tens and hundreds of amperes) enters underground a metallic construction (this is the cathodic zone and corrosion does not occurs), flows along this construction to a convenient location where it can return into the railway. This zone is the anode that corrodes proportionally to the electric current value and must be protected. Stray currents may spread tens kilometers in the soil and can cause failure over several months. This is a more dangerous corrosion phenomenon than the usual corrosion in soil. Corrosion by stray electric current can occur between the fuel pump and the fuel tank of automobiles. Alternating stray electric current is also dangerous, but less than direct electric current.

Prevention and Control of Soil Corrosion

- a. *Cathodic protection* (see Sect. 7.3). It alone does not completely protect underground metallic structures. Therefore it is used in combination with organic coatings. The combined method is recognized as the most efficient corrosion control method of underground metallic structures. Organic coatings can reduce the cost of cathodic protection while the latter can protect steel surfaces in the case of coating defects and damage. Efficient organic coatings for pipelines are *three layer coatings* consisting of a *fusion bonding epoxy* first layer, adhesive (stabilized copolymer) layer and polyolephine (polyethylene—PE or polypropylene—PP) layer (see Sect. 7.2 and Table K.6). The thickness of such coatings depends on pipeline diameter and is usually 1.5–3 mm. Polyethylene coatings

can be used up to 60 °C, and polypropylene up to 90 °C. Epoxy, polyurethane, polyurea, asphalt (bitumen), and polyvinyl chloride (PVC) coatings of thicknesses between 0.5 to 1.5 mm are also used. Coal tar coatings were widely used in previous years, but now they are not recommended for use because of their hazard properties and danger for people's health during application. Two-layer tape wrap systems and two-layer extruded polyethylene systems were widely used from the 1960s till the 1990s, but they are less efficient than three layer coatings.

High temperatures (above 80 °C) or excessive cathodic protection potentials can accelerate coating disbondment (the destruction of adhesion between a coating and the surface coated).

- b. Use of *special inert media around underground structures*. Usually 'sweet' sand (not containing salts dissolved in water) is used for filling around underground pipelines. If the soil is acidic, burnt lime (CaO) can be added for neutralization. Sometimes soil or sand is mixed with oil residues (bitumen) and in this way hydrophobic soil/sand with high electric resistivity is created.
- c. *Special methods of installation*. Pipelines and cables are installed in special concrete collectors sealed from soil.
- d. *Preventive methods against stray electric current: electric drainage* (this installation is the most effective and draws aside stray electric current from the anode zone into the railway or negative pole of the electric station); proper grounding of submerged components such as electric pumps and level gauges; prevention of electric current leakage (for instance, mounting of isolations); and special ground connections of anodic zones that are destroyed instead of underground structures.
- e. *Change of metallic underground constructions on non-metallic ones*: use of pipelines made of polymeric materials (PVC, PE, PP) or fiberglass.

The preventive anti-corrosion measure must be chosen according to the concrete local conditions.

5.8 Corrosion of Tanks Containing Petroleum Products

Aboveground storage tank (AST) is a stationary container, usually cylindrical in shape, consisting of a metallic roof, shell, bottom, and support structure where more than 90% of the tank volume is above surface grade. Underground storage tank (UST) is a stationary container, usually also cylindrical in shape, that has at least 10% of the tank volume is underground. The dimensions of AST are significantly larger than of UST. Different AST constructions exist, mostly, vertical cylindrical and horizontal cylindrical, that are diked; with fixed and floating roof tanks (Fig. 5.28).

Fixed roofs may be cone, umbrella, dome, and geodesic dome roofs. Floating roofs may be external and internal. They are built with gap (interval, space) of

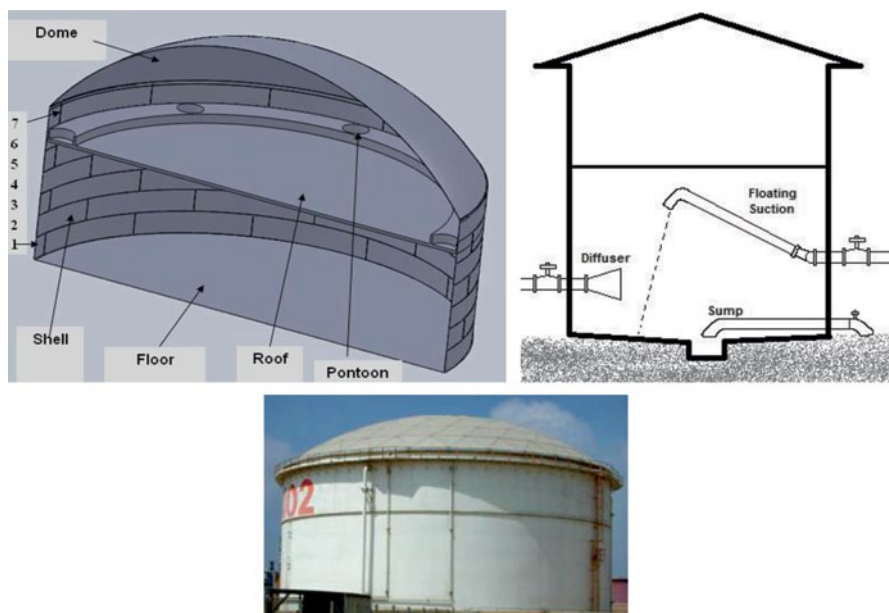


Fig. 5.28 Construction of AST (with internal floating roof). Numbers 1–7 designate strips of a shell

20–30 cm between floating roof and shell. Thus floating roof is not connected to the shell and can move up and down according to change of the level of fuel. Rim seal exists in this gap between floating roof and shell. External floating roofs may be pontoon and double deck roofs and they are subjected to influence of rains and winds (Fig. 5.29). Internal floating roofs may be pan, bulkhead pan, skin and pontoon, honeycomb, and plastic sandwich roofs. AST have different bottom types: flat, single slope, and conical (cone up and cone down). Sometimes AST have a low point on the bottom (floor), a sump, where water, bifouling and particulate are collected and removed. Some tanks have floating suction for drawing fuel off the top of the tank and not from the bottom where water, biofouling and particulate concentrate (see Fig. 5.28).

Bottom has the ‘critical zone’ that is the portion of the tank bottom or annular plate ring within 76 mm (Fig. 5.30). This zone is the immediate area of the shell-to-bottom junction (the toe of the inside shell-to-bottom fillet), maximum stress exists here and it mostly subjected to corrosion.

Analysis of corrosion failures of metallic equipment involved in corrosion incidents show that storage tanks are in the second place, after piping systems, followed by reactors, heat exchangers, valves, towers, compressors and pumps. About 20% of leakage of petroleum products is caused by corrosion in tanks [35]. General and pitting corrosion are the main corrosion phenomena inside and outside surfaces of tanks.

Corrosion in tanks may result in contaminations in fuels and their deterioration with subsequent failures of transport vehicles and unforeseen victims. Leakages

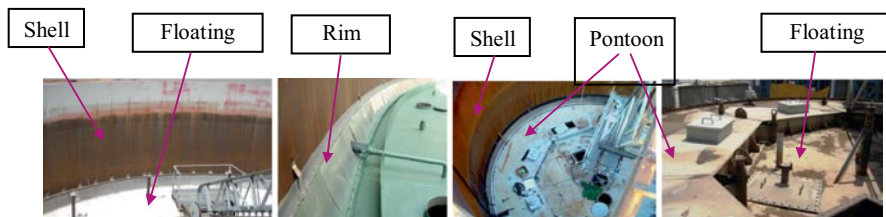


Fig. 5.29 External floating roof in AST

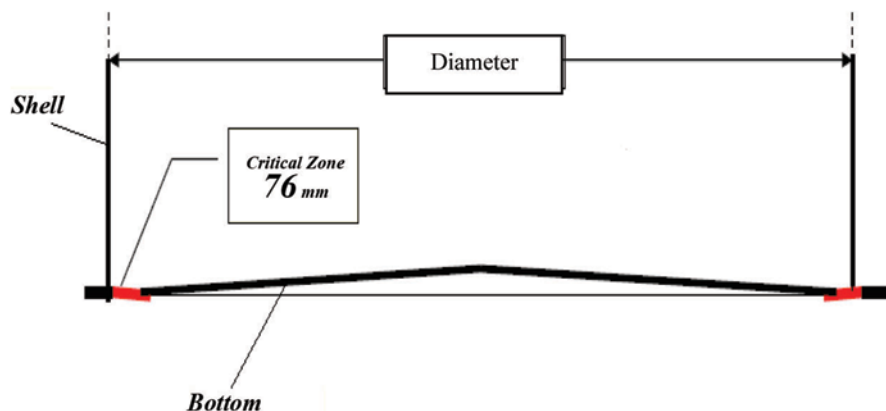


Fig. 5.30 Critical zone in AST

because of corrosion in tanks can result in loss of fuels, fires, health damage, even death of people, and dangerous environmental pollution of soil, water and air (legal and environmental claims) [36, 37].

Types of the Corrosion of Tanks The inner and outer surfaces of tanks may be subject to different corrosion types (Table 5.23).

The last two corrosion types in Table 5.23 are rare phenomena in tanks. The outer surface of the AST comes in contact with atmosphere and soil. Therefore, atmospheric and underground corrosion are responsible for the corrosion of the outer parts of AST. The outer surface of the UST comes in contact only with soil. The theory and the mechanism of atmospheric and underground corrosion are well known and understood (see Sect. 5.6 and 5.7). Therefore, effective measures are used for the prevention of corrosion of outer surfaces of roofs, shells, and bottoms (see Sect. 7).

AST containing crude oil and light petroleum products can be equipped with floating roofs and pontoons. Petroleum products may overflow (because of incorrect filling process), or rain water may fill the outer parts of the floating roofs. Spillage of petroleum products and rain water due to bad drainage through flexible hoses may result in wet corrosion of the outer surfaces of the AST floating roofs and failure of protective coatings. Groundwater and spillage of petroleum products also

Table 5.23 Corrosion types in tanks

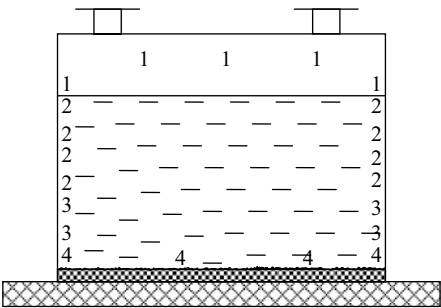
Corrosion type	Tank type location	
	AST	UST
Atmospheric corrosion of outer surfaces under rain and sunlight (under thin film of electrolytes)	+	–
Sheltered ^a corrosion of inner surfaces above the level of liquid fuels in tanks containing vapor phase	+	+
Wet corrosion (under liquid attack in the participation of dissolved water and oxygen in fuels—inner surfaces)	+	+
Underground corrosion (outer surfaces of whole UST and AST bottoms).	+	+
Microbiologically induced corrosion (AST bottoms; inner and outer surface of UST).	+	+
Corrosion under thermal insulation ^b (outer surface of AST shells).	+	–
Corrosion from stray electrical currents ^c (outer surface of whole UST and AST bottoms)	+	+
Corrosion from mechanical stresses	+	+

^aSpecific type of atmospheric corrosion (see Sect. 5.6)

^bSee Sect. 5.9

^cSee Sect. 5.7

Fig. 5.31 Corrosion zones in the inner surface of AST. [1]

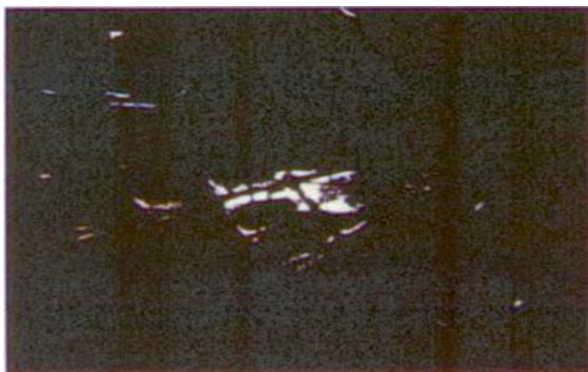


may result in wet corrosion of the outer surfaces of the UST and failure of protective coatings.

Corrosion Zones in AST The four corrosion zones are differentiated in the inner surface of AST (Fig. 5.31):

- a. A vapor zone—an upper part of inner surfaces of the roofs and shells coming in contact with vapor phase containing hydrocarbon and water vapors, and air entering inside through “breathing” valves (vents) mounted on the roofs.
- b. A splash zone—the interface between a liquid fuel and vapor phase. This boundary is not constant and the location of a splash zone changes during filling and emptying operations in AST.
- c. A wet zone—inner surfaces in contact with liquid fuel all time. The dimensions of this zone also change during filling and emptying operations in AST.
- d. A bottom zone—the bottoms and sometimes the first strips of the shell (~1 m height). These parts of some AST are in contact with aqueous electrolyte solu-

Fig. 5.32 Corrosion holes on the gas oil AST roof (inside view—one can see the sky)



tions and sludge. If the bottoms are not cleaned during much time these zones may be “dead” zones and mostly undergo corrosion.

Corrosion mechanism inside surfaces is more complicated than outside surfaces of the AST because of existence of these four corrosion zones. Corrosion intensity and its forms in AST depend on: the crude oil and petroleum product type, and, as a result, the solubility of water and oxygen in petroleum products; the volume of AST; the technology of AST exploitation (the frequency and rate of filling and emptying operations); temperature and its fluctuation; constructive features of AST (a roof type—fixed or floating, a presence of pontoon, a bottom type); an operation of the vents; condition and form of inside and outside AST surfaces (the presence of rust, coatings, etc.); the age of AST; climate (geographical location of AST; closeness to ocean, desert, and industrial enterprises); the geographical direction of AST (north, south, east or west).

Corrosion Rates in AST (Experimental Data) Usually design life of AST is 25 years. Really in practice AST may be in use significantly more: 50–70 years. Such situation requires careful analysis of corrosion state of AST. Before 1990s, many AST were used till corrosion holes formation (Fig. 5.32).

AST design, construction, corrosion control, inspection and use are influenced by regulations that have been developed because of environmental effects resulting from effluents (Appendix I).

Corrosion rates of carbon steel shells, roofs and bottoms of AST (after 55–70 years of service) containing different petroleum products are described below [38, 39]. Thicknesses of different parts of AST containing various petroleum products were measured and corrosion rates were calculated (Appendix J). These thicknesses and corrosion rates were compared with allowable minimum thicknesses (calculated according to the API Standard 653) and allowable maximum corrosion rates for different parts of AST. Thus, these measurements allow deciding about the remaining life of AST, which parts of tanks should be repaired or changed, about corrosiveness of different petroleum products in tanks during their storage, and how often we should measure thicknesses of tanks' material.

Fig. 5.33 Gasoline AST after 65 years of service (rusty and pitted inner surface of the shell)



Usually the shells of the AST are made of 7 strips with each height of 1.8 m. The numbering of the shell strips begins from the bottom—lower strip. Original thicknesses of the AST are 10 mm for bottom plates and 5 mm for roof plates. Original thicknesses of strips (depending on AST capacity) change from 18.26 mm (lower, the 1st strip) to 6.35 mm (upper, the 7th strip) (see Appendix J, Table J.1). Ultrasonic testing is used for measuring of thickness of metallic parts of tanks: bottoms, critical zones occupying 76 mm by perimeter on bottoms from shell, strips, roofs, and pontoons (see Figs. 5.28–5.30). We will describe the results of corrosion research and situation of AST containing different petroleum products and crude oil after 55–70 years of service.

Gasoline AST Gasoline AST were examined after 55–65 years of use. However, floors were replaced during this period and were in service 20 years before the last measurements of thickness.

Shell. Usually inner shell surfaces of gasoline AST are heavily rusted (Fig. 5.33).

The results of measurements of thicknesses of seven strips of the shell of typical gasoline AST and calculated corrosion rates are shown in Figs. 5.34 and 5.35.

The thicknesses of the strips 2–6 from all geographical directions are less than acceptable minimum thickness after 55–65 years of service [38, 39]. Accordingly calculated corrosion rates of the strips 2–6 are greater than acceptable corrosion rates. Corrosion rate as a function of the shell strip number is described by means of curves with maximum (0.11–0.13 mm/year) on the 3rd–5th strips. This fact is explained that the level of gasoline and accordingly floating roof most time was at the height of the 3rd–5th strips and by the scraping action of the tank floating roof rim seal which removed corrosion products from the inner surface of the shell. The service life of strips 2–6 of gasoline AST is limited to 25–30 years. It is important to emphasize that this is the planned economic life of tanks acceptable in the oil refining industry. Maximum corrosion occurs on the southern part of AST, probably, because of the most temperature fluctuations during the day-night cycle. As a

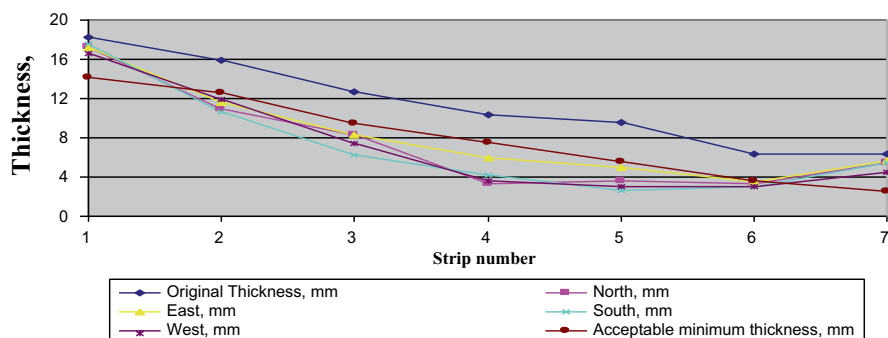


Fig. 5.34 Thickness vs strip number gasoline AST, 65 years. [39]

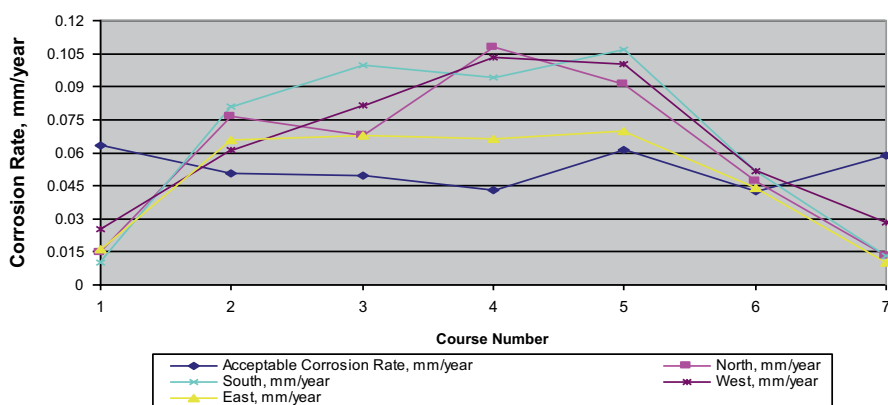


Fig. 5.35 Corrosion rate vs strip number gasoline AST, 65 years. [39]

result of direct exposure to the sunrays, the temperatures are higher on the southern part of AST, and the solubility of water increases. When the temperature decreases in night, the solubility of water in gasoline diminishes. Polar molecules of water separate from the mixture gasoline-water on the steel surface, and an electrochemical mechanism took place in the presence of dissolved oxygen (see Sect. 5.3). The inner surface of the shell mostly subjected to corrosion and therefore should be protected from it (see Sect. 7.2).

The floors of gasoline tanks are barely damaged. Corrosion rates are less than 0.1 mm/year. The critical zone is attacked more due to accumulation of water. Measuring of thickness of floors shows that the remaining life of floors in gasoline tanks is 70 years and of critical zones is 30 years. Corrosion rates of floors containing critical zones are much less than acceptable corrosion rates (Figs. 5.36 and 5.37).

Floating roofs with pontoons exist in gasoline tanks. Their corrosion rates reach 0.12 mm/year, and the service life is 20–25 years (Figs. 5.38 and 5.39). Corrosion rates of pontoons equals to acceptable values. Corrosion rates of roofs are less, but also are close to acceptable values. They should be protected from corrosion.

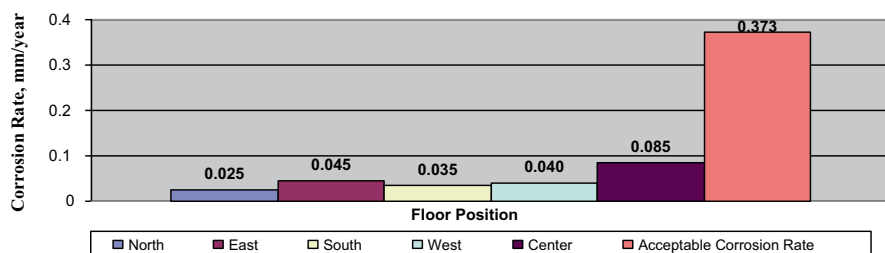


Fig. 5.36 Corrosion rate vs. floor position at gasoline AST, 20 years

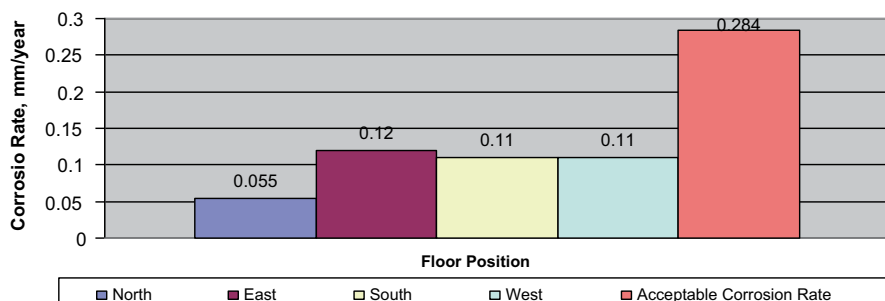


Fig. 5.37 Corrosion rate vs. floor-critical zone position at gasoline AST, 20 years

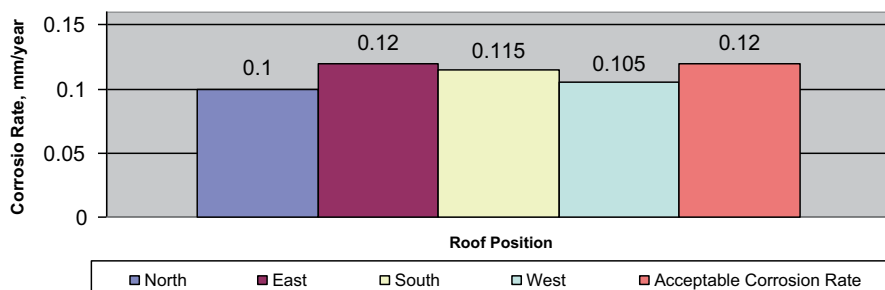


Fig. 5.38 Corrosion rate vs. pontoon position at gasoline AST, 20 years

The corrosion mechanism is probably related to the temperature fluctuations, presence of dissolved water and oxygen in gasoline and periodical water separation on the steel surface of the floating roofs and pontoons in the gasoline AST.

Kerosene AST Kerosene AST were examined after 62 years of use. However, floors were replaced during this period and were in service 20 years before the last measurements of thickness.

Shell Corrosion rates are low: 0.001–0.02 mm/year. Maximum corrosion rates occur at the strips 3–5 at the south (Figs. 5.40 and 5.41). Remaining life of shell is above 80 years. This fact points out that inner surfaces of shell in kerosene tanks do not need corrosion protection in the case that corrosiveness of kerosene will remain

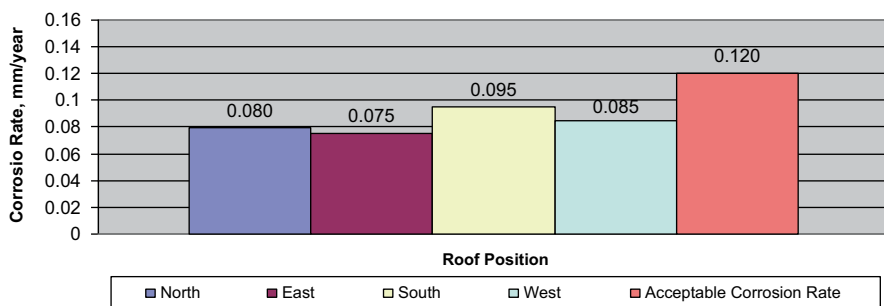


Fig. 5.39 Corrosion rate vs. roof position at gasoline AST, 20 years

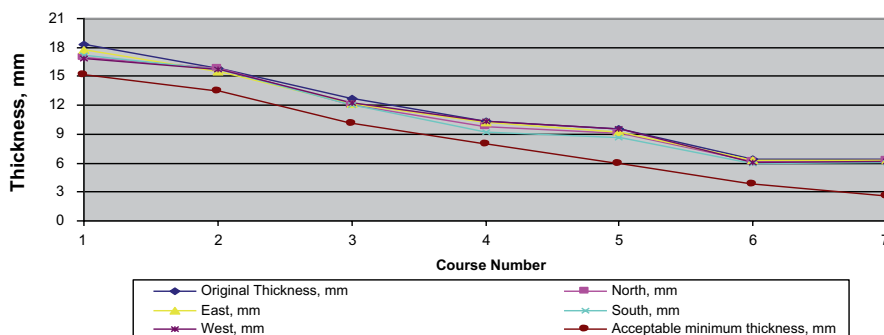


Fig. 5.40 Minimum thickness vs. strip number at kerosene AST after 62 years

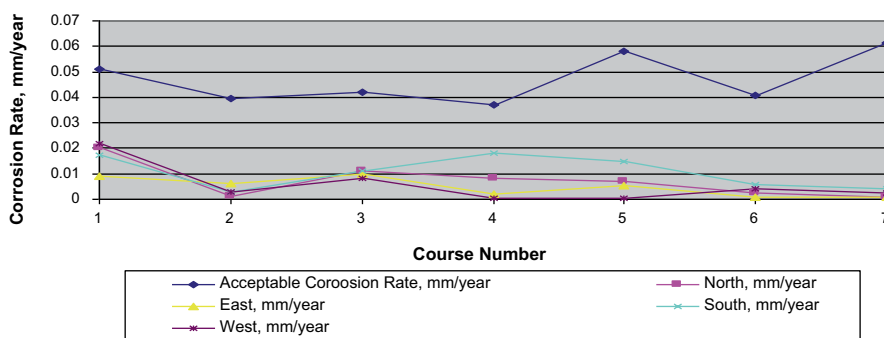


Fig. 5.41 Maximum corrosion rate vs. course number at kerosene Tank after 62 years

on the same level. However, it is recommended to measure thicknesses of kerosene tanks' shells every 20 years.

The floors in these particular kerosene tanks were in good condition because drainage and cleaning were carried out regularly. Corrosion rates equal to 0.04 to 0.11 mm/year (Figs. 5.42 and 5.43). Sometimes floors suffer from localized corrosion by microorganisms containing in the sludge. The critical zones are attacked more due to accumulation of deposits.

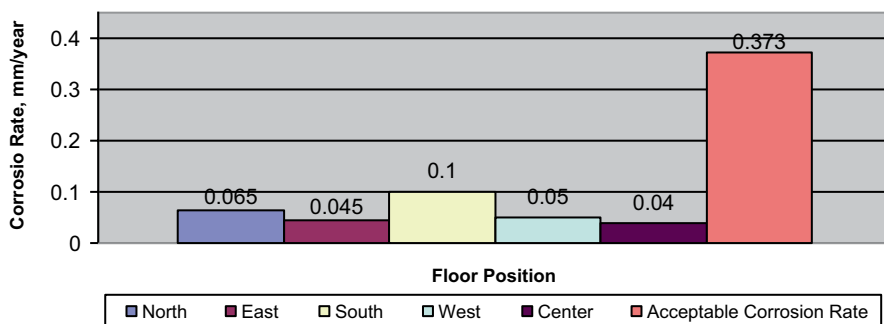


Fig. 5.42 Corrosion rate vs. floor position kerosene AST after 20 years

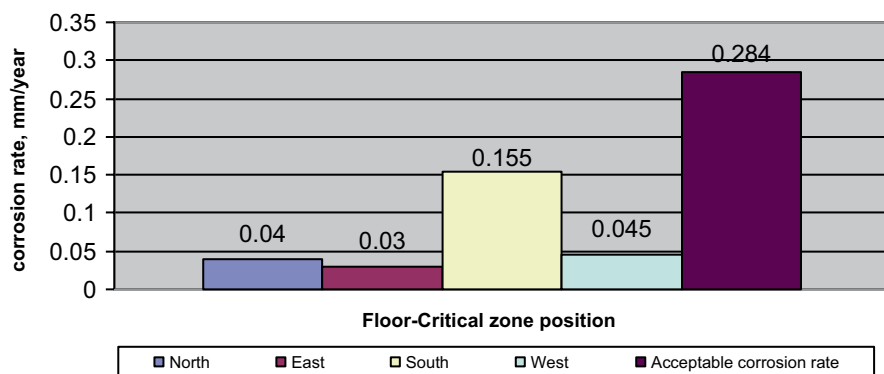


Fig. 5.43 Corrosion rate vs. floor-critical zone position kerosene AST, 20 years

Remaining life of floors is 55 years, but of critical zones is 16 years. Corrosion rates of floors including critical zones are less than acceptable values.

Gas Oil AST Gas oil AST were examined after 67 years of use. However, similar to gasoline and kerosene tanks the floors were replaced several times during this period and were in service 15 years before the last measurements of thicknesses.

The *shells* similar to kerosene tanks usually exhibit no corrosion. Corrosion rates are low and range between 0.001 to 0.022 mm/year (Figs. 5.44 and 5.45). The remaining life is more than 45 years.

Corrosion rates of *floors* are more—0.14 mm/year, but less than acceptable values (Figs. 5.46 and 5.47). Hydrogen sulphide and microorganisms containing in sludge attack the floors' surface. This means that floors should be periodically cleaned from sludge. In any case, the remaining life of floors is 38 years, and of critical zone is 22 years. If not to clean the floors from sludge they are attacked by microorganisms and shallow pits are formed reaching corrosion rate up to 0.5 mm/year (Fig. 5.48).

Fixed *roofs* exist in gas oil tanks, and their corrosion rates equal to 0.15–0.22 mm/year (Figs. 5.49 and 5.50).

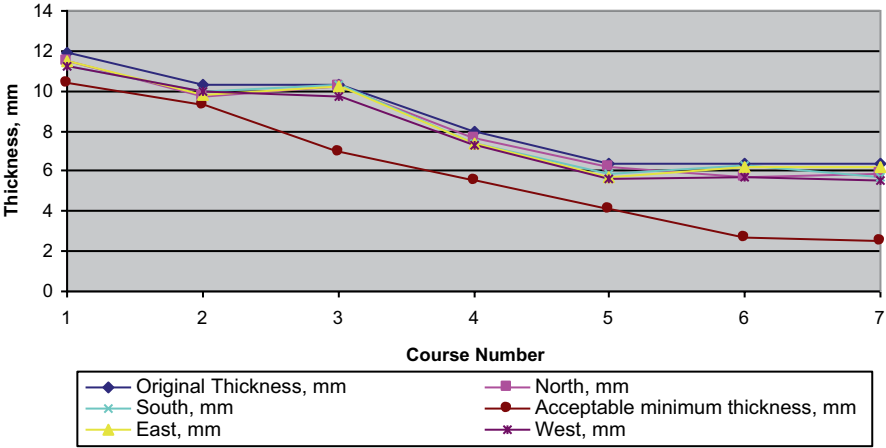


Fig. 5.44 Minimum thickness vs. strip number at gas oil AST after 67 years

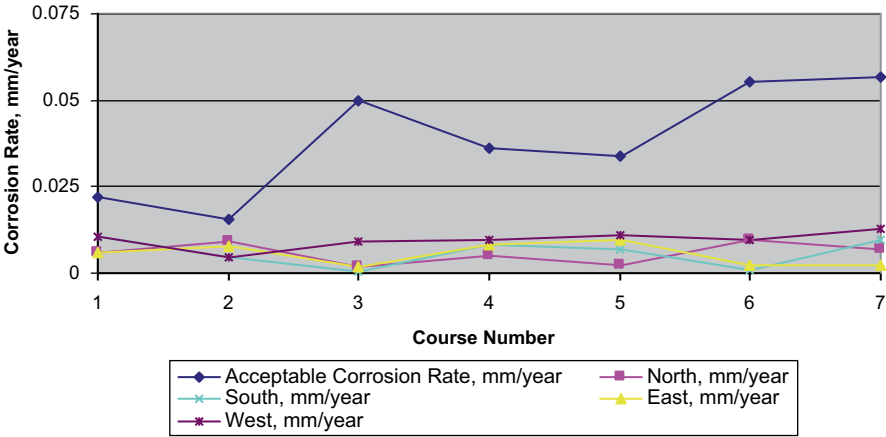


Fig. 5.45 Maximum corrosion rate vs. strip number gas oil AST, 67 years

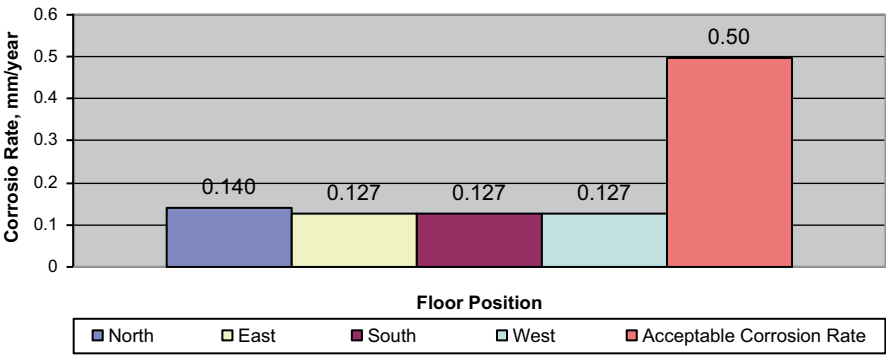


Fig. 5.46 Corrosion rate vs. floor position gas oil AST, 15 years

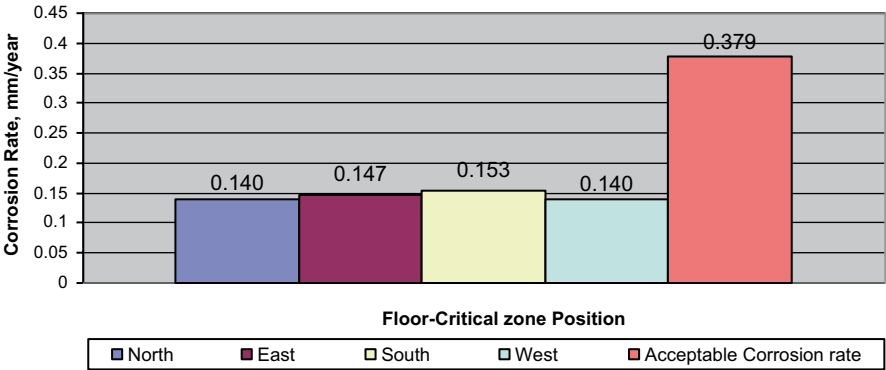


Fig. 5.47 Corrosion rate vs. floor-critical zone position gas oil AST, 15 years

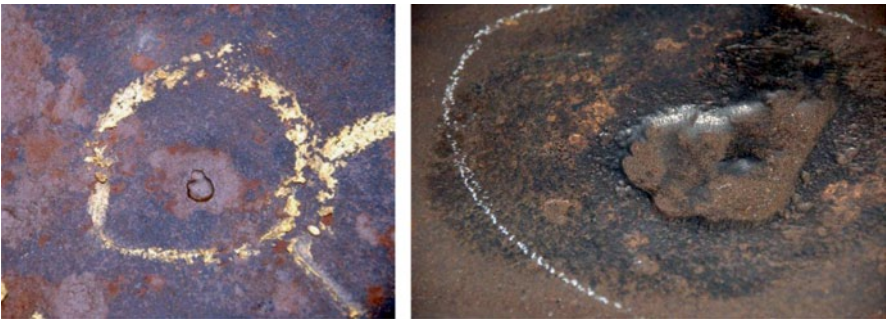


Fig. 5.48 Pitting corrosion (as a result of MIC) of inner surface at the floors of the gas oil AST

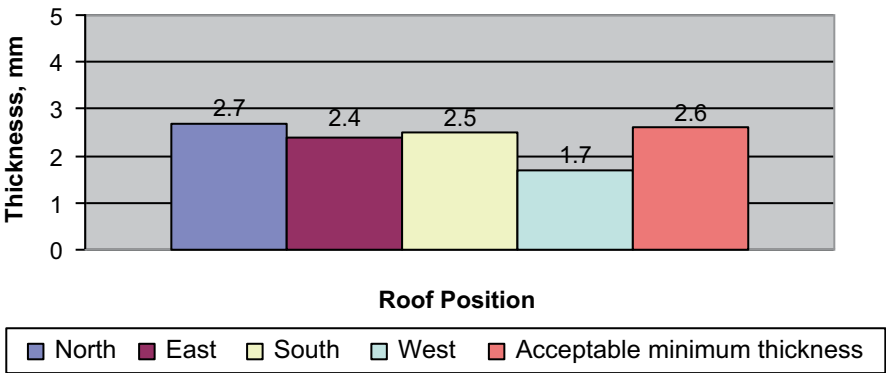


Fig. 5.49 Minimum thickness vs. roof position at gas oil AST, 15 years

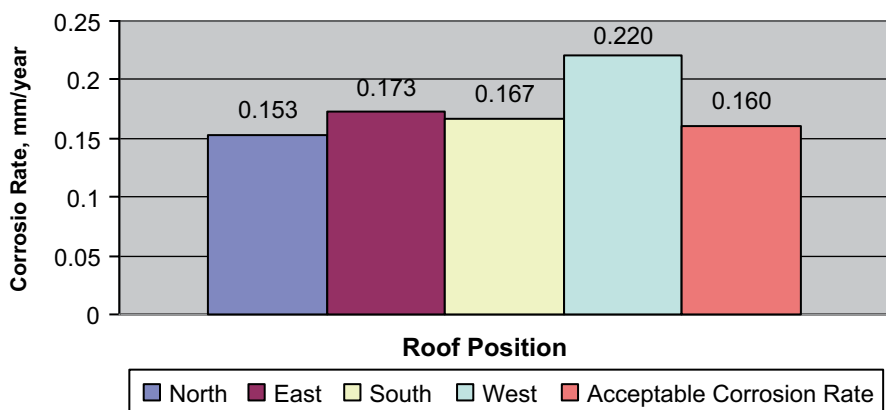


Fig. 5.50 Maximum corrosion rate vs. roof position gas oil AST, 15 years

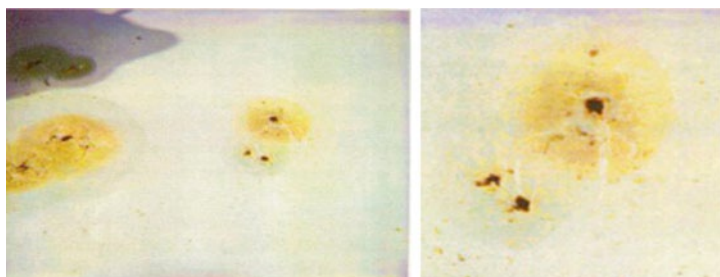


Fig. 5.51 Corrosion holes on the gas oil AST roof (*outside view*)

The inner surface of roofs is severely pitted because of attack by H_2S evolving from liquid gas oil during storage and by water vapors which are present in vapor phase under the roofs (Fig. 5.51). Pitting corrosion of roofs occur at a rate of about 1 mm/year. The service life of roofs is ~5–10 years. Corrosion rate of inner surfaces of roofs is larger than acceptable value, and roofs in gas oil tanks need corrosion protection.

Fuel Oil AST Fuel oil AST were examined after 63 years of use. Similar to gas oil tanks the floors were replaced several times during this period and were in service 15 years before the last measurements of thicknesses. Similar to kerosene and gas oil tanks, *shells* of fuel oil tanks show little corrosion with values of 0.002–0.052 mm/year (Figs. 5.52 and 5.53). There is no influence of geographic direction.

Thickness of only the first and second strips after 63 years of service is less than acceptable value. This means that the maximum corrosion rate occurs at the first and second strips and this value is greater than acceptable corrosion rate. This fact is explained by the presence of steam coil on the height of the first strip which heats

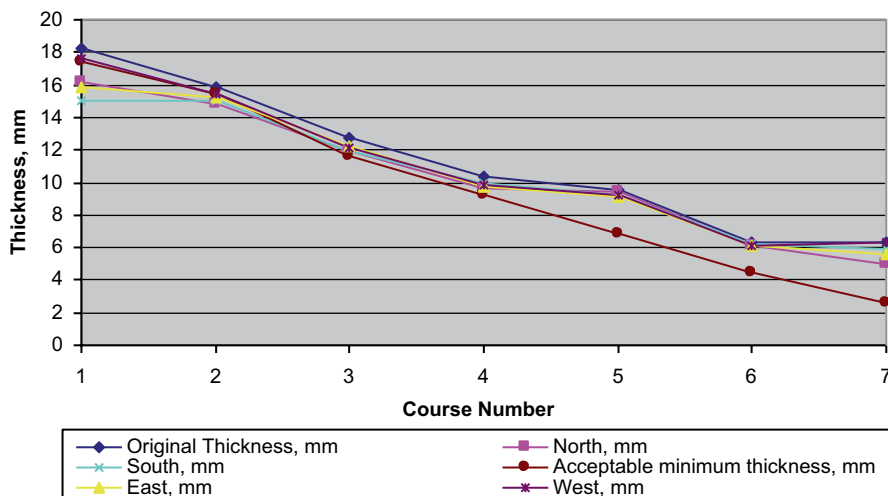


Fig. 5.52 Minimum thickness vs. strip number at fuel oil AST after 63 years

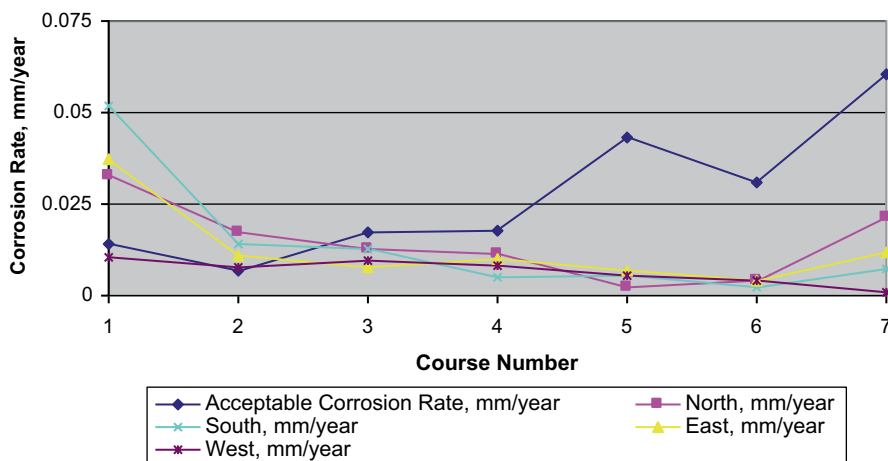


Fig. 5.53 Corrosion rate vs. strip number at fuel oil AST after 63 years

fuel oil to 90°C. The service life of the first and second strips is about 20 years, and strips 3–7 is more than 20 years.

Corrosion rate of *floors* in the fuel oil tanks is large (~0.28 mm/year), especially in critical zones (~0.38 mm/year) (Figs. 5.54 and 5.55). However, corrosion rate of floors is less than acceptable value, and that of critical zones reaches acceptable corrosion rates.

Hydrogen sulphide attacks inner side of floors with formation of holes (Fig. 5.56). The service life of floors is 26 years and 16 years of critical zones.

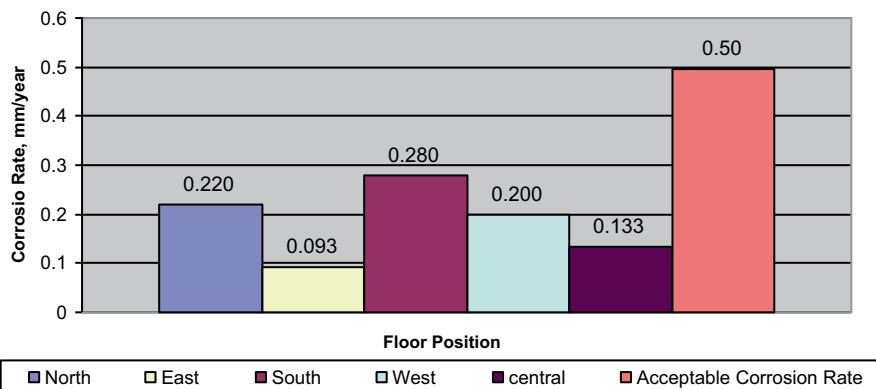


Fig. 5.54 Maximum corrosion rate vs. floor position fuel oil tank, 15 years

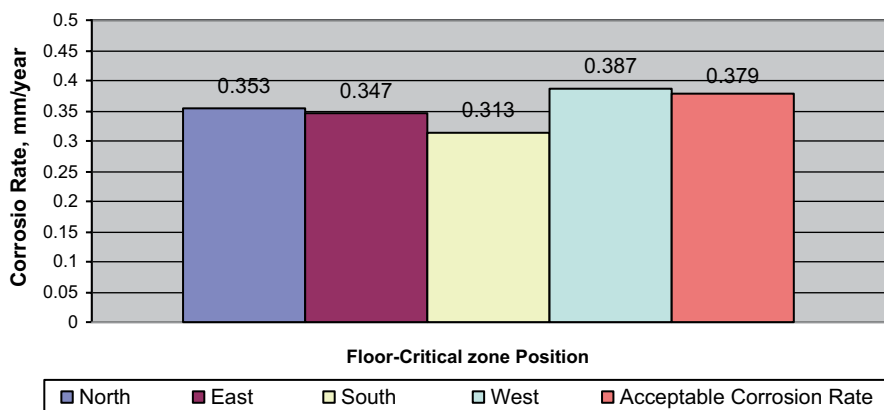
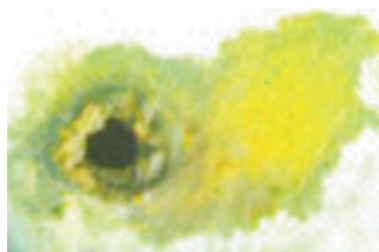


Fig. 5.55 Maximum corrosion rate vs. floor-critical zone position fuel oil AST, 15 years

Fig. 5.56 The corrosion hole in the fuel oil tank bottom



Inner surfaces of fixed *roofs* of fuel oil tanks also are attacked by H_2S which evolves from the fuel oil and by condensed water in vapor phase (similar to gas oil tanks). Corrosion products formed on the inner surface of the roof consist mainly of iron sulphides. Corrosion rates range from 0.11 to 0.18 mm/year and these values are greater than acceptable corrosion rates for roofs (Figs. 5.57 and 5.58). Service life of roofs is ~ 14 years. Usually the roofs are changed every 10–14 years.

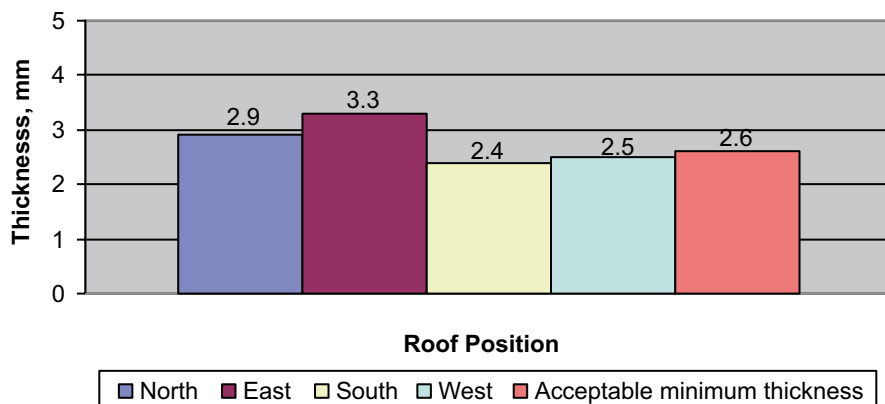


Fig. 5.57 Minimum thickness vs. roof position at fuel oil tank, 15 years

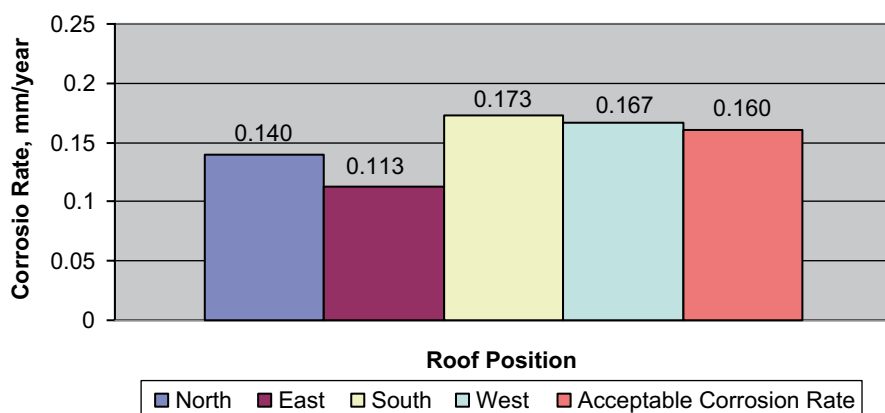


Fig. 5.58 Minimum corrosion rate vs. roof position fuel oil tank, 15 years

The main corrosion problems in fuel oil AST take place on the inner surface of the roofs and on the floors.

Crude Oil AST Similar to fuel oil AST main corrosion problems in these tanks occur on the inner surface of the roofs and on the bottoms (Fig. 5.59). Corrosion holes in crude oil AST can appear after 12–15 years of service at planning life of 25 years. Usually the roofs are repaired or changed every 15 years because of severe inside corrosion. The second region subjected to corrosion in the crude oil AST is the bottom. Usually a large quantity of sludge is formed during storage of the crude oil. For example, two meters of sludge was found on the bottom of the AST after 18 years of service [38]. Large quantities of SRB were determined in the sludge. These microorganisms were responsible for the localized attack in the bottoms. Holes of dimensions of 3 to 5 cm were revealed in the bottoms beneath the sludge



Fig. 5.59 The inner surface of the crude oil AST (20,000 m³, 18 years of service), **a** shell, **b** floating roof, **c** bottom

(see Fig. 5.59c). Usually corrosion products in crude oil AST consist of iron sulphide and rust. Corrosion rate of the bottoms can reach 0.32 mm/year.

Conclusion The causes of corrosion of different parts of AST containing petroleum products and preventive anti-corrosion measures are summarized in Table 5.24. Corrosion prevention methods of tanks are described in Sect. 7.

5.9 Corrosion of Tanks and Pipelines Under Thermal Insulation

Fuel oil and asphalt containing in tanks are heated to 100–120 °C in order to keep and transport them in liquid state. Therefore outer surface of these tanks and pipelines have thermal insulation. Sometimes steam is provided at high temperatures (120–140 °C) in small tubes made from stainless steel which also have thermal insulation. Thus, thermal insulation is used for maintaining temperature, and is intended to reduce the energy loss, controlling surface temperatures of tanks and pipes for personal protection, and preventing vapor condensation on metallic surfaces having a temperature below the dewpoint of the surrounding environment. In spite of this positive duty, thermal insulation creates conditions that cause corrosion of outside surfaces of tanks and pipes containing asphalt, fuel oil, and steam (Fig. 5.60 and Sect. 9, Case 5).

Generally, thermal insulations are divided into low temperature (under ambient temperatures of 0 to 25 °C) and high temperature (from ambient till 650 °C). Low-temperature insulations are organic foams, such as polyurethanes, polyisocyanurates, polystyrene, flexible elastomerics, and phenolics, cotton, wood, and cork. High-temperature insulations are mineral wool, fibrous glass, cellular glass (foamglass), perlite (siliceous rock, amorphous glass mineral of volcanic origin), vermiculite (natural mineral), calcium silicate, and ceramic materials. Some of them are shown in Table 5.25. Usually both low- and high-temperature insulations are porous materials which facilitate the entry and retention of water with dissolved oxygen. The main factors of corrosion under thermal insulation are tem-

Table 5.24 Corrosion causes and corrosion prevention in AST

Fuel	Part position of AST subjected corrosion	Corrosion cause ^a	Corrosion prevention method
Gasoline	Shell Roof	Dissolved H ₂ O and O ₂	Coatings (organic; metalized); Inert atmosphere; VPI; Dehumidification; Scavengers; Inhibitors (nitrites, phosphates) ^b
Kerosene (jet fuel); Gas oil (Diesel fuel)	Bottom	MIC	Drainage and cleaning; Coatings; Biocides
	Roof	H ₂ O vapors; H ₂ S; O ₂	Coatings (organic; metalized); Inert atmosphere; VPI; Dehumidification; Scavengers
Fuel oil	Bottom	MIC	Drainage and cleaning; Coatings (resistant to 90 °C)
	Roof	H ₂ O vapors; H ₂ S; O ₂	Coatings (organic; metalized); Inert atmosphere; VPI; Dehumidification; Scavengers
Crude oil	Bottom	MIC, H ₂ O, salts	Drainage and cleaning; Coatings (resistant to 90 °C)
	Roof	H ₂ O vapors; H ₂ S; O ₂	Coatings (organic; metalized); Inert atmosphere; VPI; Dehumidification; Scavengers

VPI Vapor phase inhibitor

^aThese causes result in general and pitting corrosion in AST

^bOnly for bottoms in the presence of water



Fig. 5.60 Corrosion under thermal insulation of outer surface of the pipe for fuel oil transportation. The lack of protective coating under mineral wool insulation and lack of hermeticity of aluminum jacketing caused corrosion

Table 5.25 Some Thermal Insulation Materials. [40]

Material type	Typical use	Application method	Operating temperature
Rigid polyurethane Isocyanurate	Pipelines	Shop molding or spray	to 93°C to 150°C
Polystyrene	Tank bottoms	Board stock laid in sheet form	Cryogenic to 74°C
Fiberglass	Pipes	Half shells	to 316°C
Cellular glass	Pipe/structures	Board stock/half shells	–268°C to 538°C
Calcium silicate	High temperature pipelines	Half shells	to 593°C

perature changes, type of insulation material, metal and protective coating, equipment design, weather barriers, climate, and maintenance practices. Carbon steel corrodes, not because it is insulated, but because it contacts hot aerated water. Water once penetrating under insulation, remains there for a long time, and cannot escape.

Water and oxygen are trapped on the metal surface under insulation and corrosion occurs according to electrochemical mechanism (see Sect. 5.1). Thus insulation provides a closed space for the retention of water, oxygen and other corrosive compounds. Some insulation materials may absorb water and contribute contaminants (for instance, chlorides, bromides and acids) that increase the corrosion rate. The sources of water under insulation are infiltration from outside (rain, spray from deluge systems, drift from cooling towers, condensate falling from cold service equipment, or groundwater) and condensation (during shutdowns, on cold surfaces after vapor barrier damage, or steam discharge). External water usually enters insulation through breaks in the weatherproofing. The weatherproofing breaks may be the result of inadequate design, incorrect installation, failures of jacketing, or poor maintenance practices. Condensation occurs when the temperature of the metal surface is lower than the atmospheric dewpoint. Although infiltration of external water can be reduced and sometimes prevented, insulation system cannot be made vapor tight, so condensation as a water source must be recognized in the design of the insulation system. Contaminants can increase the electrical conductivity and corrosiveness of the water media under insulation. Contaminants can be external to the insulation materials (atmospheric pollution, rains, cooling tower drift, and fire-extinguishing water deluge) and leached from the insulation materials (Cl^- , Br^- , SO_4^{2-} , and H^+). Thus external contaminants are waterborne or airborne and can enter the insulation system directly through breaks in the weatherproofing. Chlorides can be present in almost all components of the insulation system: insulation, mastic, and sealant.

Temperature significantly influences corrosion under insulation by two opposing ways. Higher temperature reduces the time water is in contact with the carbon steel surface. However, higher temperature tends to increase the corrosion rate and reduce the service life of protective coatings, mastics, and sealants.

Corrosion becomes significant for carbon steels at 0–175 °C, and for stainless steels at 50–175 °C. General corrosion is most severe at temperatures close to dew-



Fig. 5.61 Chloride SCC of stainless steel (UNS S31600) tubes under fibrous glass thermal insulation. Diameter of tubes is 12.7 mm, thickness is 1 mm. **a** General view of steam distributed system. **b** The tube with open “ends”. **c** Cracks

point (about 100°C). Corrosion rarely takes place when operating temperatures are constantly above 175°C. Tanks and bends of pipes are particularly vulnerable since they often have many nozzles and breaks in jacketing which sometimes have no suitable thermal insulation (see Fig. 5.60).

Weather barriers and vapor barriers are applied to insulation to keep it dry. Mastics and sealants are materials used to close openings around protrusions and “ends” in the insulation system. Certainly these materials must seal and protect the insulation. Their durability against mechanical abuse, ultraviolet light degradation, water, and chemicals is of prime importance. In addition, these materials must not contain leachable components that increase the corrosiveness within the insulation system.

Corrosion under thermal insulation of carbon steel is possible under any kind of insulation material. The insulation type may only be a contributing factor. Following characteristics of insulation materials influence corrosion under thermal insulation: water-leachable salts and acidic components; water permeability, wettability, and retention. For instance, some foams and fire retardants contain residual compounds that react with water to form hydrochloric or other acids.

Chloride stress corrosion cracking (SCC) of stainless steel tubes under thermal insulation can occur if chlorides are present in the environment (for instance, in rain water) and/or insulation material (even in very small concentrations, about 3–20 ppm Cl^-). When chlorides are transported with water to the hot surface of stainless steel they are concentrated by evaporation of water. Austenitic and duplex stainless steel tubes were registered failed as a result of chloride SCC. Introduction of silicates in the insulation material sometimes can prevent chloride SCC. It should be noted that silicates are not always leached out of the insulation in sufficient quantities, nor are they always in the right place to inhibit the concentrated chlorides.

The failure of stainless steel tubes (UNS S31600) under thermal insulation because of chloride SCC is shown in Fig. 5.61. Steam flowed inside of stainless steel tubes at 120–140°C and pressure 3 bar. Fibrous glass insulation contained 16 ppm Cl^- . Rainfalls (containing 3 ppm Cl^-) entered through open “ends” under insulation. In addition, chlorides were leached from the insulation material. Chlorides were concentrated on the outer surface of stainless steel tubes under insulation and caused SCC after 3 months of service. When stainless steel is used an insulation material must be free of chlorides. In order to prevent penetration of rains the ends must be “closed” with silicone mastic.

5.9.1 Prevention of Corrosion Under Thermal Insulation

- a. Use of appropriate coatings before tanks and pipes are insulated: organic (high-build epoxy, fusion-bonded epoxy, epoxy phenolic, epoxy novolac, silicone hybrid), aluminum metalizing (thermally sprayed), and wax-tape coatings (Appendix L, Tables L.4 and L.5). Use of organic coatings is limited by operating temperature. For instance, high-build epoxy, fusion-bonded epoxy and wax-tape coatings are used up to 60 °C, epoxy phenolic to 150 °C, epoxy novolac and silicone hybrid to 205 °C. Thicknesses of these coatings vary from 200 to 400 μm . Thermal-sprayed aluminum coatings of 300–375 μm thickness may be used up to 595 °C. All organic coatings are used both on carbon and stainless steels. Inorganic zinc-rich coatings are not suitable because they are not resistant in closed, wet environment under insulation. Insulation cannot prevent the ingress of water, air, and contaminants from outside sources, therefore use of coatings resistant to water at high temperatures is of critical importance.
- b. Careful and correct design. The most effective measure is to keep the insulation in dry form. The only non-water absorptive insulation is a cellular glass. Insulated systems must be designed in such a manner that corrosives are minimized, that is to lessen the intrusion of water. Generally, thermal insulation has lagging, or jacketing, providing mechanical and weather protection for the insulation. The materials that are used for jacketing are aluminum, aluminized steel, and galvanized steel. It has to be taken into account that galvanized steel, or zinc coatings are not resistant to an industrial atmosphere containing hydrogen sulphide and other sulphur-containing gases. Mastics, sealants, and caulks must not contain polyvinyl chloride, brominated compounds, and acetic acid derivatives because they can cause SCC of stainless steel. Introduction of silicates in the insulation material can prevent chloride SCC of stainless steel.
- c. Careful regular inspection: visual examination and removal of insulation, ultrasonic thickness measurement, radiography, acoustic emission, eddy current, X-ray transmission, magnetic flux leakage, infrared examination, and neutron backscatter.
- d. Correct maintenance. Insulation systems are disturbed for repairs and are not properly reinstalled and sealed, allowing water ingress under insulation. Expansion joints have also to be given special attention because they are susceptible to uncontrolled movement and failure of insulations.

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Chapter 6

Polymeric Materials in Systems for Transportation and Storage of Fuels

Look around... We entered the Polymer Age...

The author.

Abstract Polymeric materials are used in different application in contact with fuels, fuel oxygenates, aromatic solvents (BTX), biofuels (bioalcohols and biodiesel) and rain water. Composite materials also are used as coatings for corrosion prevention of inner surfaces of AST containing crude oil and fuels. Ignorance of knowledge about resistance of polymeric and composite materials to fuels and wrong use can result in their destruction and deterioration of fuels and environment. Polymers and their properties are described. Their classification according to generic nature, thermal processing behavior and mechanical behavior is explained. Thermoplastics, thermosets and elastomers are described. Swelling mechanism of polymers with liquid fuels is explained in detail. Rating of polymers according to swelling in fuels is analysed. Resistance of polymers to fuel oxygenates and aromatics, aggressiveness of biofuels (bioalcohols and biodiesel) to polymers is described. Experimental data of swelling of 16 polymers in diesel fuel, blend B10 and neat biodiesel B100 are given and analysed. Elastomers compatible with biofuels are recommended.

Polymeric materials are used in different application in contact with fuels, fuel oxygenates, aromatic solvents (BTX), biofuels (bioalcohols and biodiesel) and rain water. Sealants, hoses and bonded flexible pipes made from polymeric materials also can contact fuels. Pipelines for transportation crude oil/fuels, UST and pits can be made from composite materials. Composite materials also are used as coatings for corrosion prevention of inner surfaces of AST containing crude oil and fuels. The secondary containment of tanks can be made from polymeric materials. Due to different chemical and complicated composition of fuels and biofuels the resistance of polymeric materials also varies. Ignorance of knowledge about resistance of polymeric and composite materials to fuels and wrong use can result in dramatic effects: their destruction and deterioration of fuels and environment (Fig. 6.1). Presence of aromatics in fuels can drastically influence resistance of polymers (see Fig. 6.1e).

Sometimes insufficient mechanical properties of polymeric materials or their wrong storage in the atmosphere of oil refineries also can result in failures (Fig. 6.2).

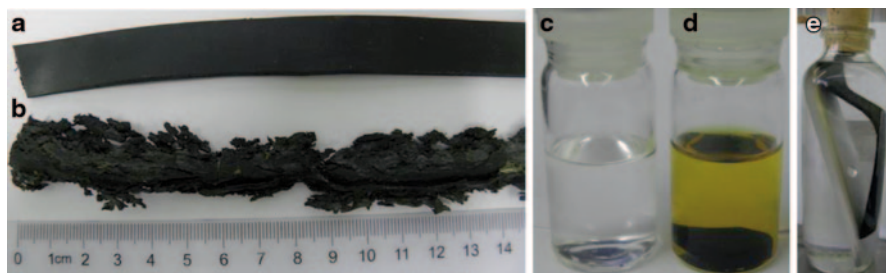


Fig. 6.1 **a** A seal (original) made from natural rubber (isoprene), **b** A seal from isoprene after 6 months of service in contact with kerosene, **c** Original kerosene, **d** Kerosene after 1 day of contact with isoprene, **e** Separation of the gasket made from cross-linked polyethylene from aluminum surface after 2 h of immersion in toluene



Fig. 6.2 Flexible hoses made from NBR (Nitrile Butadiene Rubber, Buna N) for water drainage from the AST roof outside after contact of outer surface with fuel oil at 90 °C after 5 years of service (**a**), with gasoline after 3 years of service (**b**), and with industrial atmosphere (sunlight, rain water, oxygen) after a year of storage (**c**).

In hoses, a specific point is that the inner lining polymer and the outer cover polymeric material are exposed to two very different environments—rain water inside and fuel (or aromatics or oxygenates) outside respectively. Material selection must reflect this, especially regarding liquid compatibility, but also involving material strength, crack-resistance and resistance to fatigue for the cover, and which might be subject to impacts during service.

In order to understand which polymeric materials can be used in contact with specific fuels (especially containing aromatics and oxygenates) and biofuels (bioalcohols and biodiesel) we will be familiar with general properties of polymers

6.1 Polymers and Their Properties

Polymer is a material consisting of repeating units (group of atoms). The amount of these groups can vary from hundreds to tens of thousands units. The properties of polymers as well as other materials depend on the composition and structure. Sometimes polymeric materials are called plastics or plastic materials. This is misuse because plasticity is related to the property of a material, and not only polymers but metals also can be plastic under certain conditions. Three classifications are used

for the description of polymeric materials: according to *generic nature*, *thermal processing behavior*, and *mechanical behavior*.

Generic nature is the chemical organic family to which polymers belong. Examples are fluoropolymers, vinyls, epoxies, polystyrene, etc.

Thermal processing behavior of polymers is thermal characteristics, namely, how polymers react on temperature change. According to thermal characteristics, polymers are classified into *thermoplastic* and *thermosetting*.

A *thermoplastic* polymer is a polymer that becomes pliable or moldable above a specific temperature, and returns to a solid state of needed form upon cooling. In other words, *thermoplastics* can be remelted and reprocessed somewhat like metals can be melted and refrozen into new shapes. Therefore *thermoplastics* also are called *thermosoftening polymers*. They are usually either a semi-crystalline or glassy amorphous materials. Examples are polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), fluoropolymers, and vinyls. We can compare behavior of *thermoplastics* with plasticine. Therefore, correctly to say only *thermoplastics* can be named “plastics”. Thermoplastics are used in flexible underground piping, sumps, and vapor recovery tubing.

A *thermosetting* polymer is a polymer which is built like network and can not be fusion and recycling. Examples are vulcanized rubber, epoxies, etc. Thus *thermosetting* polymers (named also *thermosets*) are solid polymer materials with rigid cross-linked structures, and when heating to high temperature they are decomposed and charred. Thermosets are glassy materials and generally stronger than thermoplastics due to three dimensional network of bonds (cross-linking), and are also better suited to high-temperature applications up to the decomposition temperature. However, they are more brittle. Thermosets are used in reinforced composites and as matrix materials for rigid piping, UST, and protective coatings.

According to *mechanical properties*, polymers are classified into rigid, semi-rigid, and nonrigid polymers. Semirigid and nonrigid polymers possess by high elongation and high recovery. They are called *elastomers*. An *elastomer* (*elastic polymer*) is a polymer with viscoelasticity. Viscoelasticity is the property of materials that exhibit both viscous and elastic characteristics when undergoing deformation. Rubber is an example. Therefore, *elastomers* also termed *rubbers*. They are characterized by the following features:

- a. Ability to stretch up ten times of their initial length.
- b. Elastomers strain instantaneously when stretched and just as quickly return to their original state once the stress is removed at ambient temperatures.
- c. Ability to extend and contract many times.
- d. When elastomers are stretched they reveal strength and resistance to further deformation.

In other words, elastomers are deformable, largely resilient and reversibly elastic, soft, and are able to maintain constant volume on deformation. These properties are specific only to elastomers and do not exist in other materials. For instance, steel can elongate by elastic deformation only up to 1%, and when steel is stretched greater than 1% it elongates without ability to return to initial length. We should

apply force 1 million times more in order to stretch steel wire of the same length as elastomer wire. Owing to their properties elastomers are used in components that are required to be deformable and flexible, for instance, in flexible hose constructions, seals, gaskets, and packing.

Complete description of a polymeric material must include its generic nature, thermal processing method, and classification of its mechanical properties. For instance, hoses used in tanks are NBR, thermosetting, and rigid; Viton used for seals is fluoropolymer, thermosetting, and elastomeric.

Polymeric materials are characterized by their mechanical, thermal, electrical properties, and chemical compatibility. Temperature significantly influences all properties of polymers. When heated, chemical degradation may occur. When cooled, polymers can become stiff and brittle. Each polymer has its own temperature characteristics. We mostly are interested by chemical compatibility of polymers and composites to fuels: swelling, softening, weight gain/loss, chemical attack, and degradation.

Swelling of polymers If the macromolecules in polymer are randomly oriented and entangled, then the material is termed “amorphous” (e.g., elastomers at room temperature). In contrast, some polymers are capable of closely-packed self-organization to acquire crystalline domains with three-dimensional order; these polymers (e.g., polyethylene) are referred to as “semi-crystalline”. The remaining non-crystalline regions are amorphous. Internal “free volume” exists within amorphous regions giving rise to chain flexibility, if not restricted by neighboring crystalline regions. Elastomers are an amorphous class of polymer. Paradoxically, however, the very root of the flexible nature of polymers, particularly elastomers, reflecting the existence of the free volume through which macromolecules can move when stressed, also provides the “Achilles heel” for attack by external liquid components contacting a polymer. If available free volume were not there, the liquid could not enter the polymer matrix, but the polymer would be rigid—as essentially applying to many thermosets. After liquid has entered, the free volume is reduced but not eliminated; subsequently, kinetic movements of chain segments then allow some regeneration of free space (often eventually causing the polymer to swell). Any liquid (consisting of small molecules) contacting polymers can be absorbed into polymers. Swelling is absorption of liquids resulting in excessive stress if constrained (e.g., seal) or excessive deformation and weakening of the polymer if unconstrained. A small amount of swelling can be beneficial, e.g. in low pressure gas line seals and abandonment permanent plugs.

Different additives (plasticizers, heat stabilizers, processing aids, antioxidants, etc.) are commonly added to polymeric materials in order to achieve a certain needed property set. For instance, plasticizers work by embedding themselves between the chains of polymers, spacing them apart, increasing the free volume and the plasticity (flexibility) of polymers. By the way, the “new car smell” is caused mostly by plasticizers evaporating from the car interior. These additives are generally not chemically bonded to the polymer and are able to migrate. If a polymer containing additives comes in contact with a solvent, the additives may be extracted by the solvent. Extractable plasticizers are generally low molecular weight esters and are most commonly used in elastomers such as Buna-N (NBR) and flexible thermo-

Table 6.1 Rating of polymers according to swelling in fuels [1]

Swelling, % vol.	Effect on polymers' properties
<10	Little or no effect
10–20	Possible loss of physical properties
20–40	Noticeable change
>40	Excessive change

plastics such as PVC and PA (Nylon). They are, however, much higher molecular weight than the constituents in oxygenated gasoline. Extraction of plasticizer results in increase of free volume in polymer, solvent enters inside and polymer swells. Often the polymer will swell through a maximum value then begin to shrink as the plasticizer leaves the host material. Therefore the effects of plasticizer extraction may not be observed until the polymer is removed from the solvent allowed dry-out for several hours or days. Extraction of plasticizers leads to shrinkage and increasing the brittle-ductile transition temperature of polymer. Shrinkage of seal materials can compromise their sealing behavior. For instance, oxygenate MTBE is capable of extracting solid fillers, such as titanium dioxide. Alcohol blends loosen fibers from the fiberglass filler. Even in relatively dilute alcohol blends, considerable loss of stiffness and strength are caused by plasticization for many polymeric materials.

In addition to extraction of additives from polymer and its swelling, the liquid may chemically attack the polymer surface initially, and continuing inside its bulk after absorption to cause further deterioration in properties and performance of the polymer part. Chemical degradation is chemical changes due to attack by a contacting liquid. High temperature will soften polymers, increase the rate of diffusion of liquids and gases and accelerate chemical degradation. Since thermosets possess by large amounts of cross-linked bounds which prevent penetration small molecules of solvent and thus they practically do not swell. Composites (rigid materials) are composed of thermosets and rigid glass fibers and as a result they also possess very low swelling. Diffusion of solvents in and through polymers is generally accompanied by a change in properties of the material. In addition to the change in physical dimensions associated with swelling, mechanical properties (strength, stiffness, hardness, and tear resistance) are usually affected. Therefore it is important to define the acceptable volume swell of polymers in fuels. It is suggested the rating of influence of swelling on polymer's properties (Table 6.1).

Certainly these values are considered general rules and depend on service application. As little as 20% vol. swell can reduce the mechanical properties of an elastomer by 60%. Twenty to twenty five % vol. swelling is generally considered an upper limit for solvent absorption by an elastomer in a sealing application [2, 3]. Polymers are considered fuel resistant (for static O-ring applications where the O-ring is not compressed against a moving surface) if the volume swell percent is less than about 30% [4]. For example, the volume swell of NBR is 34% in gasoline and in gasoline containing 10% MTBE (see Appendix K, Table K.10). NBR is used with success as sealing material in contact with neat and oxygenated (MTBE) gasoline. The maximum decrease 40% in tensile strength of polymers after immersion in solvent is considered as allowable value [3].

Increasing the ether content in gasoline generally increases the swelling response of elastomers monotonically and their swelling behavior may be predicted. By contrast, increasing alcohol content in gasoline generally produces a maximum swelling response in polymers. This maximum is located at approximately 15 % vol. ethanol and somewhat higher for methanol. Such difference in dependence of swelling on concentration of ethers and alcohols is explained by the fact that ethers form ideal solutions with gasoline, while alcohols form non-ideal solutions prone to separation. Generally, an alcohol-gasoline blends are more aggressive toward polymers than any of the neat constituents in the fuel (see Appendix K Tables K.8 and K.9).

6.1.1 Permeability of Polymers

Any solvent which can absorb into a polymer will also permeate through it. The permeability of polymer is measured by mass (in gram) of solvent which penetrates through polymeric material of 1 mm thickness and area 1 m² in unit of time (per day). Generally, the presence of oxygenates accelerates permeation of hydrocarbon fuels in polymers. Among ethers, MTBE may be more permeable than other oxygenates. Alcohols, particularly methanol, permeate better than ethers. The less molar weight of alcohol the permeability is greater.

Greater permeability is observed in elastomers (hoses, seals, gaskets, packing) relative to thermoplastics (flexible piping, sumps, vapor recovery, tubing) and composites (rigid pipes, tanks, coatings). In general, fluorinated elastomers and thermoplastics offer better permeation resistance than nonfluorinated materials.

6.2 Resistance of Polymers to Fuel Oxygenates and Aromatics

Ethers (MTBE, ETBE, and others) and alcohols (methanol, ethanol, and others) are fuel oxygenates (see Sect. 3). Ethers in amounts to 15 % vol., methanol and ethanol to 3–5 % vol. are added to gasoline. However, alcohols themselves also are used as fuels and they can be blended with gasoline in any ratio (see Sect. 4).

Resistance of polymers to ethers and aromatics is described in this section and Appendix K. The behavior of other group of fuel oxygenates (alcohols) will be discussed in Sect. 6.3 and Appendix K.

Many polymer materials, such as Viton, NBR, epoxy and polyurethane coatings, are resistant to pure gasoline, but some of them fail in gasoline when new chemical compounds are added. For instance, aromatic solvents (BTX) are not corrosive to metals but are aggressive to most polymers and organic coatings. Therefore all polymers and organic coatings which were examined for resistance in contact with gasoline before the use of fuel oxygenates and aromatic solvents adding nowadays to gasoline, must be examined in gasoline with these new components once more.

The results of examination of resistance of different polymers in gasoline, BTX, fuel oxygenates and their mixtures with gasoline are given in Appendix K. The swelling values of fluoroelastomers change very little with the addition of either alcohols or ethers to gasoline whereas swelling usually increases for most other thermoplastics. Increasing the fluorine content in fluoroelastomers generally improves its resistance to swelling and permeation by oxygenates. Increasing acrylonitrile content in NBR improves its resistance to aromatics as well as its permeability to gasoline. Higher acrylonitrile content in NBR has a lesser beneficial effect on the resistance to ethers and actually reduces the resistance of the NBR to fuels blends containing large concentrations of ethanol and methanol.

6.3 Aggressiveness of Biofuels to Polymers

Properties of biofuels (alcohols and esters) were described in Sects. 4 and 5.5. Because of polarity of alcohols and esters (biodiesel) they possess increased ability to penetrate into some polymers and wash away various components into solution and thus deteriorate the physico-chemical properties both of biofuels and polymers. Biofuels are organic solvents and their properties depend on their nature. They can dissolve some polymeric materials, organic deposits and lacquers formed in fuel storage tanks and pipelines previously successfully used for conventional fuels. Most organic coatings which were examined and are used in contact with traditional fuels are unsuitable for use in contact with biofuels. Increase of amount of alcohol in gasoline and biodiesel in conventional diesel fuel usually enhances solvent capability of blends. Chemical degradation, swelling, softening, delamination, permanent deformation, blistering, shrinking, and discoloration of some polymers in biofuels in contrast to conventional fuels may occur. Such degradation of polymers, for instance, can impair their ability to seal joints (see Fig. 6.1).

The presence of alcohols and biodiesel in conventional fuels facilitates also the permeation of hydrocarbons through certain elastomers and thermoplastics, and to a significantly lesser degree in thermosetting polymers.

Biofuels can influence adversely in a number of ways on polymers. Elastomers and thermoplastics are susceptible to permeation and swelling which can result in leaks and failure (due to brittleness or stiffening). Fluoroelastomers usually are more resistant to these problems, but have also experienced low temperature failures in fuel ethanol due to stiffness. Seals, hoses, injectors, and filters made from polymeric materials are planning for use in contact with biofuels during 20 year design life. Therefore in order to choose polymers they must be immersed and tested under laboratory conditions during period not less than 20–30 days. Some standards require to 365 days of immersion of thermosets at ambient temperature [5] and to 180 days of fiberglass at 50 °C [6]. Sometimes initiation period is needed to penetrate organic liquids inside of polymers. It is needed to measure the changes of weight of polymers with time of immersion to reaching their constant weight. The absence of changes in weight of polymers points out that equilibrium conditions have been

established. The time required reaching equilibrium absorption or steady state permeation (for the same solvent and temperature) depends on the type of a polymer and its thickness. For instance, usually fluoroelastomers require much more time to reach equilibrium absorption than polymers containing only carbon and hydrogen atoms. The diffusivity and permeability of fluoroelastomers to solvents is correspondingly lower. The resistivity of polymers to alcohols and biodiesel is different. We will describe separately the resistance of polymers to alcohols and biodiesel.

6.3.1 Aggressiveness of Alcohols to Polymers

Swelling of polymers is enhanced by alcohols through the various associations possible among solvent-solvent and polymer-solvent interactions. Neat methanol may exist as a hydrogen-bonded cyclic tetramer. Both single methanol molecule and associated molecules exist in equilibrium. Single methanol molecule is quite polar; whereas methanol existing as a tetramer, is considerably less polar. For this reason, self-associating dry methanol is a powerful swelling agent for both polar and, surprisingly, non-polar polymers alike. Small quantities of added water tends to break-up the tetramer methanol species and lower swelling is observed for fluoroelastomers (e.g., Viton) in hydrated methanol. A mixture of gasoline with alcohol upsets the typical hydrogen bonding of alcohol and sets loose polar groups within the blend that attack polar compounds of polymers [4]. Unfortunately, many polar compounds that provide polymers with resistance to hydrocarbons are highly vulnerable to polar groups (-OH) of alcohols, especially methanol and ethanol. Fuel additives and cosolvents generally are not effective in mitigating the attack. IPA, TBA, and MTBE do not seem to exhibit these solubility and polar effects on polymers [4]. Polymers' compatibility with gasoline-alcohol blends are given in Tables 6.2, 6.3 and Appendix K.

Flexible piping manufacturers use liners of polymeric materials PA-12 (Polyamide), PA-11, PVDF, and PA doped PE to provide compatibility with the alcohol-gasoline blends. Sumps are constructed of either FRP or PE. Cross-linked PE (PEX, thermoset) is preferred over HDPE (thermoplast) as it is stiffer, more chemically resistant, and has better low temperature impact. Generally, methanol fuel blends are more aggressive than ethanol fuel blends towards polymers.

6.3.2 Aggressiveness of Biodiesel to Polymers

Resistance of polymers to biodiesel depends on its origin. As a rule biodiesel blends B20 and lower have much smaller influence on polymers than neat biodiesel B100. Small concentrations of biodiesel in B2 and B5 have no noticeable influence on polymers.

When we are talking about some generic or brand type of polymer, e.g., Viton, we should note that different types of Viton exist and they contain different amounts

Table 6.2 Recommended polymers for use in gasoline-alcohol blends^a [7–9]

Alcohol	Polymeric materials
Methanol, Ethanol	NBR ^b (hoses and gaskets) ^c
	CIIR ^d (hoses and gaskets) ^c
	Viton ^{e,f}
	Teflon and some other fluoropolymers
	Nylon ^g
	EPDM rubber
	Neoprene
Methanol	Acetal
	Fluorosilicone ^f
	Polysulphide rubber
Ethanol	Polyethylene ^f
	Urethane coatings ^h
	Ethylene acrylic acid polymer coatings
	Polypropylene

^a Gasoline-Methanol blends contain co-solvents (ethanol, propanols, or butanols)

^b NBR (Nitrile Butadiene Rubber, Buna-N, Nitrile)

^c Gaskets seal a connection between two components that have flat surfaces, while seals are used between engine parts that rotate. Seals tend to be flat and round, while gaskets are often cut into different shapes so that they fit the components

^d CIIR (Chlorine isobutylene-isoprene rubber; Butyl rubber, Neoprene rubber)

^e Viton—Highly fluorinated elastomers; trade name of fluoropolymer elastomers (DuPont Dow Elastomers)

^f These materials can lose some properties in contact with pure methanol. Therefore they must be examined in contact with particular blend

^g Resistant at $T < 30^{\circ}\text{C}$

^h May be suitable for splash service but not long-term immersion
Ceramics are resistant to fuel ethanol

of fluorine (usually between 66 and 70 wt%) and other ingredients (see Appendix K). The greater content of fluorine is in Viton, the more it is resistant to biodiesel, alcohols, ethers and their blends with fuels. Thus Viton B (68 wt% fluorine) and Viton F (70 wt% fluorine) are more resistant even to acidic biodiesel. Viton is generally compatible with petroleum products (hydrocarbons), but incompatible with organic acids (e.g., acetic acid) and ketones (e.g., acetone). Results of experiments of resistance of 16 widely used polymeric materials to diesel fuel, blend B10 and neat biodiesel B100, are shown in Fig. 6.3 and summarized in Table 6.4.

Elastomers Nylon, Polyethylene, Polypropylene, Viton, Teflon, fluorosilicone rubber and NBR (Buna-N, Nitrile) are compatible with diesel fuel, blend B10 and neat biodiesel B100 (see Table 6.4).

Neoprene (CR, synthetic rubber, also called polychloroprene or chloroprene) and Hypalon (CSM, Chlorosulphonated polyethylene) are resistant to conventional diesel fuel and blend B10, but are not resistant to neat biodiesel B100. Rubbers EPDM (Ethylene Propylene Rubber), Butyl Rubber, NR (Natural Rubber), IIR (Chlorobutyl Isobutylene Isoprene Rubber), and Silicone Rubber are not resistant to diesel fuel, blend B10, and neat biodiesel B100.

Table 6.3 Not recommended polymers for use in gasoline-alcohol Blends^a [7–9]

Alcohol	Not recommended polymeric materials
Methanol, Ethanol	NBR ^b (seals) ^c CIIR (seals) ^c ABR ^d AU ^d
Methanol	Polyurethane ^c
Ethanol	Natural rubber Epoxy PVC Polyamides Methyl-methacrylate Leather Cork EU ^d

^a Gasoline-Methanol blends contain co-solvents (ethanol, propanols, or butanols)

^b NBR (Nitrile Butadiene Rubber, Nitrile, Buna-N)

^c Gaskets seal a connection between two components that have flat surfaces, while seals are used between engine parts that rotate. Seals tend to be flat and round, while gaskets are often cut into different shapes so that they fit the components

^d P. A. Schweitzer, Mechanical and Corrosion-Resistant Properties of Plastics and Elastomers, Marcel Dekker Inc., USA, 2010, p 492

ABR polyacrylic rubber, *AU* polyester based polyurethane, *EU* polyether based polyurethane

^e These materials loss some properties in contact with pure methanol. Therefore they must be examined in contact with particular blend

Table 6.4 Swelling^a (% vol.) of 16 polymers in diesel fuel, blend B10 and neat biodiesel B100

Polymer	Swelling, % vol.		
	Diesel fuel	B10	B100
Nylon	0.36	0	0.12
Polyethylene	1.44	0.96	0.58
Polypropylene	2.40	1.68	1.05
Viton ^b	0.36–0.84	0.36–0.81	0.8–6.7
Teflon ^b	0.24–5.41	0–5.0	0–4.9
Fluorosilicone	2.7	2.7	5.5
NBR	2.9	3.1	15.0
Neoprene 60	7.5	11.4	54.6
Neoprene 50	11.0	16.9	73.7
Hypalon (CSM)	11.8	17.5	65.6
Silicone rubber ^b	52.9–88.9	55.1–92.7	19.8–27.4
EPDM 75	96.5	93.1	48.8
Butyl rubber	137.0	139.0	70.9
NR (Natural rubber)	149.5	164.0	155.0
IIR (Chlorobutyl)	195.0	198.0	118.8
EPDM 60	269.5	263	107

^a Experiments were carried out by the author according to ASTM 471-12A [10] during 24 days at 22 °C

^b Swelling (% vol.) ranges for Viton, Teflon and Silicone rubber of different types and manufactures

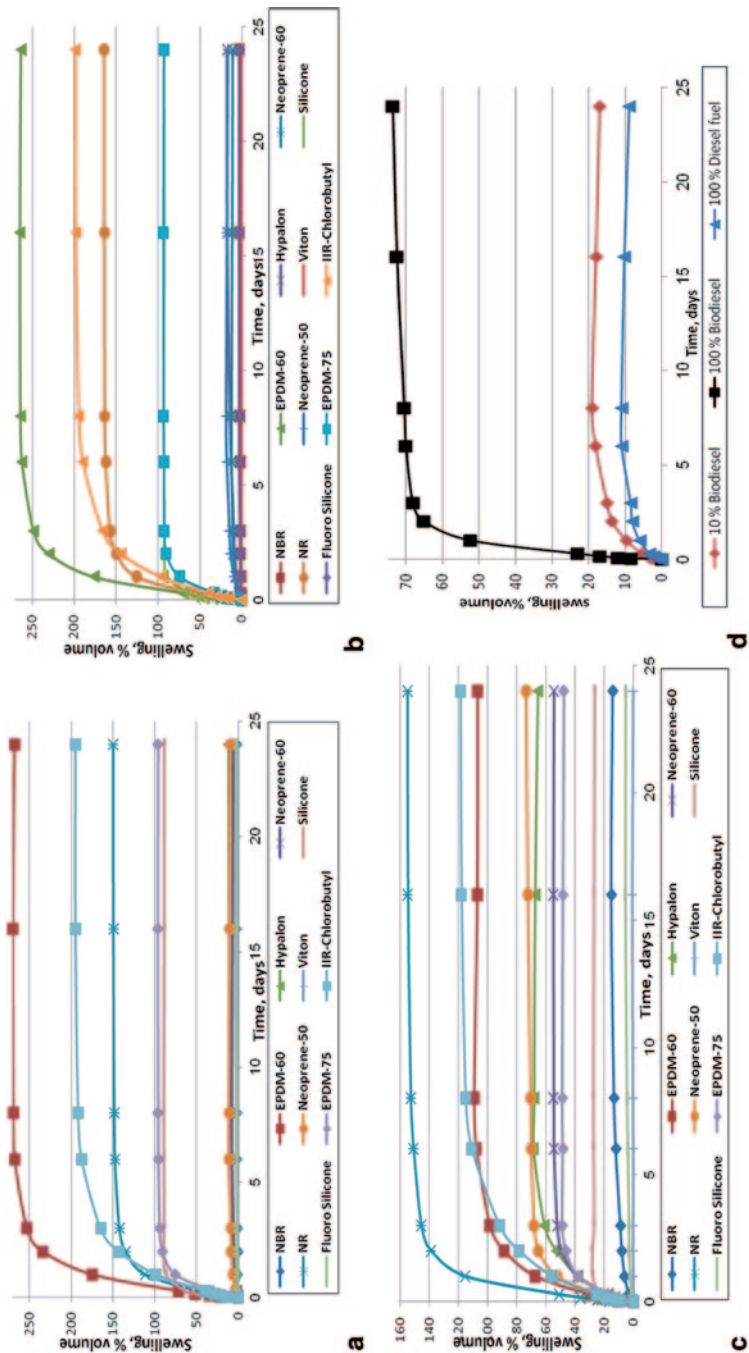


Fig. 6.3 Kinetic curves of polymers' swelling (% vol.). **a** Diesel fuel, **b** Neat biosol **c** Blend B10, **d** Neoprene 50 in three types of fuel. T = 22 °C

We should keep biodiesel spills wiped up because it can remove some types of paints if the fuel is not wiped up immediately. It can also remove decals that are stuck on tanks or vehicles near the fuel areas. It is advisable to inspect visually the equipment once a month for leaks, seeps, and seal degradation.

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Chapter 7

Corrosion Prevention and Control in Systems Containing Fuels

*Smart will always find a way to solve the problem,
But a wise man never enters it.*

Jewish folk wisdom.

Abstract Anti-corrosion preventive measures of systems for transportation and storage fuels must be started at the stage of engineering design and correct use of standards. Preventive methods can be divided into three groups: measures dealing with metals (selection of materials), measures dealing with the environment (treatment of fuels, atmosphere, and water), and measures dealing with the interface metal–environment (use of coatings and cathodic protection).

Selection of materials means design and use of metals/alloys, polymeric and composite materials compatible with fuels and other environments. Organic and metallic protective coatings for tanks and pipelines containing fuels are described in detail. Among them non-conductive and antistatic coatings for anti-corrosion protection of inner surface of AST containing gasoline, naphtha, and other petroleum products, coating systems for protection of outer surface of AST, of underground and submerged pipelines, and metalizing coatings. Recommendations for the examination and selection coating systems under the conditions of fuel storage tanks are given. Experience of anti-corrosion protection of inner and outer surfaces of AST is described. Cathodic protection of the external surface of AST bottoms, underground storage tanks (UST), underground and submerged pipelines also is described. Corrosion inhibitors in liquid and vapor phases are discussed and recommended. Antibacterial treatment, technological and combined measures of corrosion control, secondary containment and double bottom, and UST use are described.

Anti-corrosion preventive measures of systems for transportation and storage fuels must be started at the stage of engineering design and correct use of standards (Appendix I). Design of compatible materials, hydrophobic basement (foundation) for AST, constructions with as little as possible crevices, suitable coatings, systems for injection of corrosion inhibitors, scavengers of corrosion substances (H_2S , H_2O , O_2), biocides, and cathodic protection systems are viable. It is important also to design and to plan corrosion monitoring methods which will be able to follow up the state of materials, the corrosiveness of the environment, and the efficiency of anti-corrosion control measures. All this must be carried out during (at the stage of)

design, erection of tanks and pipelines, creation of equipment intended for contact with fuels and their use.

Three main factors influence corrosion: a metal type, the environment, and conditions at the interface between a metal and the environment. Therefore, we can use the properties of a metal, of an environment, and of a border metal–environment for corrosion control measures in systems containing fuels. In the light of this, preventive methods can be divided into three groups: measures dealing with metals (selection of materials), measures dealing with the environment (treatment of fuels, atmosphere, and water), and measures dealing with the interface metal–environment (use of coatings and cathodic protection).

Selection of materials means design and use of metals/alloys, polymeric and composite materials compatible with fuels and other environments. Corrosion preventive measures dealing with the environment are based on treatment of fuels, atmosphere, and water, namely, on fuel composition and impurities in it, as well as on the composition of vapor and aqueous phases which can be present in tanks and pipelines containing fuels. These measures include removal the corrosive components by a suitable procedure, for instance, drying, deaeration, removal H_2S and chlorides, use of corrosion inhibitors, and anti-bacterial treatment. In the case of conventional fuels (gasoline, kerosene, diesel fuel, and fuel oil), drying may be effective. In biofuels, the elimination of small amounts of water will not influence corrosion appreciably, however, if water fully will be removed this will result in significant decrease of corrosion. On the other hand, there are systems (for instance, aluminum in boiling methanol and ethanol) where drying is dangerous because aluminum loses its passivity. In the case of H_2S or organic sulphur-containing compounds in fuels, removal of these corrosive compounds is a successful anti-corrosion preventive measure. Deaeration by purging of an inert gas (nitrogen or argon) of biofuels will reduce participation of dissolved oxygen in corrosion and thus will prevent corrosion, for instance, SCC of carbon steel in fuel ethanol.

We should add technological measures the performance of which may significantly diminish and prevent corrosion in most cases. Anti-corrosion preventive measures of systems for transportation and storage fuels are described below.

7.1 Choice of Materials

Liquid fuels are stored in tanks and are transported through pipelines, ships, ocean tankers, barges, railroad tank cars, and tanker trucks. AST sometimes are equipped with floating roofs and pontoons. Sometimes one type of fuels is changed by another in tanks and pipelines; sometimes tanks and pipelines are used for the single fuel. In the first case, fuels can intermix. In this case pigging is used to provide a barrier between different liquid fuels that use the same pipeline. Pigs are usually made of polymeric material polyurethane foam. Pipelines are best suited for transporting large amounts of fuels. Fuels can be transported also by truck, railcar, or barge because of their smaller volumes. Ships, barges, rail tank cars, and tank trucks are

compartmentalized, so in cases of multiproduct transport, different fuels are physically prevented from intermixing. Sea water can be used for filling tanks in ship tankers for ballast. In these cases, remaining sea water can be mixed with fuels. In some cases, the compartments are dedicated to a single fuel. In other cases, residue of the fuel previously transported in a compartment may be mixed with the loaded fuel. Physico-chemical resistance of all constructive materials is very important in preserving environment and fuels from deterioration. We will describe materials which are used in contact with fuels.

Metals and Alloys Carbon steel, stainless steel and aluminum alloys are used as materials of AST, UST, pipes, truck tanks, car tanks, ship tanks, tankers, railroad tanks, floating roofs and pontoons, pumps and their components (rotors, etc.), filters, hydrants, dispensers, etc. Materials used in the construction of tanks should comply with API 620, API 650 and they may be carbon steel, austenitic stainless steels 304, 304 L, 316, 316 L, 317, and 317 L, duplex stainless steel, and aluminum. The duplex stainless steel may be SAF 2205 (UNS S31803), 2003 (UNS S32003), 2101 (UNS S32101), SAF 2205 (UNS S32205), 2304 (UNS S32304), Ferralium alloy 255 (UNS S32550), 255+ (UNS S32520), SAF 2507 (UNS S32750), and Zeron 100 (UNS S32760). Chemical content of alloys is given in Appendix H.

Carbon steel and stainless steel are named ferrous alloys because iron is the main component. Other alloys (based on aluminum, copper, etc.) are called nonferrous alloys.

Carbon steel is an alloy containing iron (Fe) and carbon (C) at concentrations from 0.008 to 2 wt%, and small amounts of other elements (Mn, Cr, Ni, Mo, Cu, Si, S, P). Generally tanks and pipelines are made from low-carbon (mild) steel (Fe+0.1 to 0.3 wt% C). Nowadays low-carbon steel ASTM A516 Grade 70 (UNS K02700) is widely used as a material of AST and UST. Carbon steel has the advantage of lower capital cost. The disadvantage of carbon steel constructions is higher life cycle cost due to increased maintenance and costs associated with corrosion protection.

Stainless steel is used for manufacturing new small tanks, car tanks, and as details of floating roofs in AST. *Stainless steel* is an alloy of iron with chromium content above 12 wt%. Tenacious passive film chromium oxide (Cr_2O_3) is formed on stainless steel surface and is responsible for protective properties in pure atmosphere, water, and fuels. Stainless steels UNS S30400 (Fe+18 to 20 wt% Cr+8 to 12 wt% Ni) and UNS S31600 (Fe+16 to 18 wt% Cr+10 to 14 wt% Ni+2 to 3 wt% Mo) usually are used in fuel systems. Stainless steel is prone to localized corrosion: pitting, crevice, and SCC (see Sect. 5).

Aluminum alloys are used for manufacturing floating roofs, pontoons and fixed roofs in AST (geodesic dome). Aircraft store fuel in their wings made from aluminum alloys. Each tank in wings has a pump that supplies fuel to a manifold that feeds engines.

Aluminum and *zinc* are used as metalizing protective coatings on inner surfaces of truck tanks and stationary tanks (capacity 5–50 m³) made of carbon steel. Zinc coatings also are used for protection of outer surfaces of truck tanks. Filter/separators are made from aluminum or carbon steel (coated by epoxy paint).

Aluminum is a metal resistant to aqueous solutions with $\text{pH}=4.3\text{--}8.3$. This pH range depends on chemical content of the solution and temperature. Aluminum is an amphoteric metal and corrodes in more acidic ($\text{pH}<4.3$) and more alkali ($\text{pH}>8.3$) media. Aluminum is resistant to hydrocarbons, hydrogen sulphide, acetic acid, and disodium silicate solutions. The tenacious aluminum oxide (Al_2O_3) film that forms on the aluminum surface is responsible for protective properties in a wide range of environments. Pure aluminum without oxide film dissolves in methanol and ethanol (see Sect. 5.5.1). Because aluminum and its alloys are lighter (density of aluminum is 2.7 g/cm^3) than most other metals and alloys (density of carbon steel is 7.9 g/cm^3) it is the obvious choice for tanks' domes and transportation (aircraft, high-speed trains). The mechanical strength of aluminum may be enhanced by cold work and by alloying; however, both processes tend to diminish resistance to corrosion. Principal alloying elements include copper, magnesium, silicon, manganese, and zinc. Aluminum and its alloys are susceptible to general, pitting, crevice, galvanic corrosion, SCC, and MIC.

Zinc is a metal resistant to aqueous solutions with $\text{pH}=6\text{--}12$. This range depends on chemical content of solution and temperature. Similar to aluminum, zinc is an amphoteric metal and corrodes in more acidic ($\text{pH}<6$) and more alkali ($\text{pH}>12$) media. Zinc is resistant to hydrocarbons but is not resistant to hydrogen sulphide and ammonia.

Pumps and their components (casings, rotors) may be made of *cast iron* or *bronze*. Fittings, valves, and gauges may be made of *brass*.

Cast iron is an alloy containing iron, carbon (1.8–4.5 wt%), silicon (2 wt%) and manganese (0.8 wt%). Cast iron contains much carbon, therefore it is brittle. Although it is brittle, it is fine for low-stressed components like cylinder blocks, pistons, and drain pipes. They are produced by casting. Cast iron melts more easily than steel (adding carbon reduces the melting point in just the way that adding anti-freeze works with water) and this makes the pouring of the castings much easier. Usually corrosion resistance of cast iron is similar to that of carbon steel in most environments.

Copper is soft and ductile metal, corrosion resistant to many environments and a good electrical conductor. The mechanical and corrosion-resistant properties of copper may be improved by alloying (addition of some elements).

Brass is an alloy consisting of copper (70–60 wt%) and zinc (30–40 wt%). Brass is stronger than copper, is much easier to machine. Brass is susceptible to dezincification (selective leaching of zinc) under particular conditions, pitting corrosion, and SCC.

Bronze is an alloy consisting of copper (90–70 wt%), tin (10–30 wt%) and sometimes aluminum (11 wt%), zinc (2 wt%), silicon, phosphor, and nickel. Bronzes are somewhat stronger than the brasses, yet they still have a high degree of corrosion resistance to many environments.

Copper and its alloys are not resistant to media containing hydrogen sulphide and ammonia.

Special requirements exist for materials in contact with jet fuel. For instance, galvanized steel (steel with zinc coating), zinc, copper and their alloys are not rec-

Table 7.1 Resistance of NBR, Viton and Teflon in gasoline, BTX, MTBE and their mixtures with gasoline

Media		Polymer		
		NBR	Viton	Teflon
Gasoline	Neat (100%)	R	NR	R
	+ 15 % vol. MTBE	R	NR	R
	+ 35 % vol. BTX	NR	R	R
BTX (100%)		NR	R	R
MTBE (100%)		R	NR	R

R recommended (resistant), *NR* not recommended (non-resistant)

ommended for use in contact with jet fuel because copper and zinc may catalyse oxidation of jet fuel and thus deteriorate its quality.

Polymeric Materials (see Sect. 6 and Appendix K) The choice of polymeric materials depends on the purpose of their use. Flexible pipes (hoses) using for the drainage of rain water from the roofs of AST are made from polymeric materials. Outer surface of these pipes is in contact with fuels, oxygenates, aromatic solvents, and biofuels. Inner surface of these pipes is in contact with rain water. Usually Buna-N (NBR) or Viton are used for flexible hoses. Seals (O-rings, gaskets, packers, plugs, repair clamps), washers and nuts, tubing, fuel returned lines, valve sleeves, flexible joints, diaphragms, pulsation damper bladders and bellows, protective coatings, adhesives, foams, films, thermal insulators and insulations of electrical wiring using in tanks, pipelines, pumps, and filters contacting fuels and their components also are made from polymeric materials. Mostly NBR, Teflon, and Viton are used for these articles.

High density polyethylene (HDPE) is used as membrane material for secondary containment (see Sect. 7.8). However, polyethylene and polypropylene are not recommended as construction materials for very long contact with petroleum products. Recommendations regarding use of polymers in gasoline, MTBE, BTX and its mixtures are given in Table 7.1.

Recommendations of polymers' compatibility with gasoline-alcohol blends and biodiesel blends are given in Sect. 6.3. Polymers using in fuel systems are described in Appendix K.

Composite Materials All materials using in constructions and devices are classified into three groups: metals, polymers, and ceramics. *Composite materials* (in short *composites*) are a combination of two generically dissimilar materials brought together for synergy where one phase (termed *matrix*) is continuous and surrounds the other phase (often called the *dispersed phase* or *reinforcement*) which is discontinuous. Reinforcement can be in the form of particulates, fibers or cloth. A *composite* is multiphase material and its properties are the function of the properties of the constituent phases, their relative amounts, and the geometry of the dispersed phase. The properties of *composite* are improved relative to properties of

constituent phases. There are natural and artificial composites. For instance, bone is a composite of the strong yet soft protein collagen and the hard, brittle mineral apatite. Wood consists of strong and flexible cellulose fibers surrounded and held together by a stiffer material lignin. Concrete is a composite material consisting of two ceramic materials, a coarse aggregate (gravel) and a fine aggregate (cement). Using the high strength of fibers to stiffen and strengthen a matrix material is probably very old. The Processional Way in ancient Babylon was made of bitumen reinforced with plaited straw. Straw and horse hairs have been used to reinforce mud bricks for at least 5,000 years.

Other examples of composites are *fiber reinforced plastic* (FRP; named also *fiberglass*), filled fluoropolymer gaskets, scrim-filled elastomers for gaskets and impoundment basin liners. Polymers can be filled with glass particles, sand, or silica flour, increasing the stiffness and wear-resistance. Many composites are based on epoxies, though there is now a trend to using the cheaper polyesters.

Fiberglass first became a viable alternative to protected steel, in 1950. That year centrifugal cast fiberglass piping was first used in the crude oil production industry as a solution to corrosion problems. Fiberglass is used for manufacture UST, rigid pipes for crude oil/fuels transportation, and protective coatings inside AST. *Fiberglass* also is called *glass-reinforced plastic* (GRP) or *glass-fiber reinforced plastic* (GFRP). It is made of a polymer matrix reinforced by fine fibers of glass. Its bulk strength and weight properties are also very favorable when compared to metals, and it can be easily formed using molding processes. A polymer matrix may be polyester, vinyl ester, epoxy or polypropylene. Fiberglass is resistant to crude oil, fuels, and ethers. As a resin using in the fiberglass may be different its resistance to methanol and ethanol can also changed. Therefore any fiberglass must be examined for compatibility with alcohols before use under particular conditions.

7.2 Coatings

Organic and metallic coatings are used as protective coatings for tanks and pipelines containing fuels.

Organic coatings found the widest use among all protective methods of inner and outer surfaces of AST and UST containing fuels, as well outer surfaces of underground and submerged pipelines for fuels transportation. The use of protective coatings allows not only to prevent corrosion in tanks, but to maintain the quality of fuels, to reduce losses of volatile organic components of fuels (thus protect the environment and keep fuel quality), and to reduce wear of pontoons and seals in floating roofs. The coefficient of friction may be much larger for a corroded surface than a coated steel surface. Therefore the rim seal life may be significantly extended if the shell is coated. The requirements to coatings using inside of AST are: resistance to all fuel components, abrasion resistance (because of movement of floating roofs with pontoons), resistance to cold and hot water (90 °C) and surfactants (during cleaning of AST), and coatings should not affect the fuels physico-chemical properties (quality) during long period of contact (storage).

The use of organic coatings for protection of inner surfaces of AST for fuels were started in about 1915 and to 1950–1960's rich experience with advantages and drawbacks was accumulated. Before the 1940's following coatings were examined: gunite (concrete lining), vinyl (precursor of PVC), alkyds, shellac, air dried and baked phenolics, litharge, and minium. The vinyl and gunite coatings gave the best results and their use continued from the 1930's into the 1950's and 1960's. The service life of gunite coatings was about 15–20 years. However, following drawbacks of gunite coatings were detected: large weight of dense concrete, rapid wearing and deterioration of the seals of pontoons and floating roofs, and difficulties in gas (hydrocarbons) freeing of fuel AST (because of porosity of gunite), resulting in safety problems. Phenolic-aluminum and inorganic zinc rich silicate coatings were used in 1940's. Coating systems based on epoxy, such as coal tar epoxy, epoxy amine, epoxy polyamide, and epoxy phenolic coatings, were started to use in 1960's. Polyurethane coatings were examined in the same time. Fiberglass Reinforced Plastic (FRP) coatings with thickness 1,600 μm were started to use in the mid-1950's.

The API RP 652 standard [1] recommends two types of coating systems for the protection inner surfaces of bottoms in AST: thin ($< 500 \mu\text{m}$) and thick ($> 500 \mu\text{m}$). The recommended thin coating systems are coal tar epoxy, epoxy phenolic, epoxy amine, epoxy polyamide, and epoxy polyamidoamine. The coal tar coatings during application are harmful to people and the environment. Thick-film coatings consist of a glass-reinforced lining based on polyesters (isophthalic, bis-phenol-A, vinyl ester), or epoxy resin. Glass reinforcement includes flake, chopped strand, mat, and roving. For new tanks or for older tanks where only internal corrosion is occurring, 900–1,400 μm thick coatings may be used. For older storage tanks where bottoms have corroded both internally and externally, 2–3 mm thick glass-reinforced (FRP) coatings are often used.

Gasoline can contain oxygenates (for instance, MTBE to 15 % vol.) and aromatics (BTX to 35 % vol.). The following coatings were examined and recommended for anti-corrosion protection of an AST containing gasoline (with MTBE or BTX) and other fuels (Appendix L): inorganic zinc silicate; epoxy; polyvinyl chloride; silicone-epoxy; epoxy phenolic; epoxy novolac; polysiloxane; polyurethane; epoxy reinforced with glass and mineral flakes; glass-filled epoxy with rust converter, inhibitor, and passivator; vinyl ester with acrylic copolymer; epoxy vinyl ester, and vinyl ester. Nowadays epoxy coatings are mostly used for anti-corrosion protection of inner surfaces of AST containing fuels. Hybrid cycloaliphatic epoxy coatings (100 % solids, non-solvent) with thickness 0.5–3 mm are developed which can be applied even at -18°C [2, 3].

Organic Coatings for Gasoline-Alcohol Blends Gasoline-alcohol blends can extract an epoxy coating from a gasoline storage tank. A practice was established to store these blends in unlined tanks. Urethane coatings are resistant for splash exposure to such blends. However, they may not be appropriate for liquid immersion service. The coating based on ethylene acrylic acid copolymer provides good resistance to gasoline-alcohol blends.

7.2.1 *Antistatic Coatings for Anti-corrosion Protection of Inner Surface of AST Containing Gasoline and Naphtha*

AST containing gasoline and naphtha are furnished with floating roofs. During movement of these roofs static electricity can accumulate on the inner surface of shell (see Sects. 2 and 5.3.1). In addition to general requirements to coatings using inside of AST these coatings should be *antistatic* or *electro-conductive*. Coatings intended to protect the inner surface of the gasoline and naphtha AST are divided into three groups according to the values of electrical resistance R of coatings: electro-conductive coatings ($R < 10^3 \Omega$); antistatic coatings ($R = 10^4 - 10^5 \Omega$), and non-conductive (dielectric or electrical insulators) coatings ($R > 10^6 \Omega$). Coatings shown in Appendix L, Table L.1 meet all above mentioned requirements except that they are non-conductive coatings and are intended for use inside of AST containing kerosene (jet fuel), gas oil (diesel fuel), fuel oil, and crude oil. Most countries have no requirements that the coatings inside of AST containing gasoline should be antistatic or electro-conductive. In such countries, non-conductive coatings shown in Appendix L, Table L.1 may be used. However, there are some countries where standards require use of antistatic or electro-conductive coatings inside of AST containing gasoline. Earthing (grounding) of AST does not prevent formation of static electricity on the inner surface of organic coatings during the movement of gasoline in tanks. Powders of aluminum, zinc, nickel oxide and graphite are added to conventional paints to increase their electrical conductivity and turn them into antistatic or electro-conductive coatings. The generic types of these coatings are epoxy (with solvent and solventless), epoxy phenolic, epoxy containing special electro-conductive pigments, and zinc rich coatings. Abrasion resistance of epoxy and epoxy phenolic coatings is higher than that of zinc rich coatings. These antistatic and electro-conductive coatings should be used for protection of inner surfaces of shells and floating roofs of AST containing gasoline and naphtha (see Appendix L, Table L.2), though unfortunately non-conductive coatings are used significantly more often.

7.2.2 *Coating Systems for Protection of Outer Surface of AST Containing Crude Oil and Fuels*

Coatings intended for protection of outer surface of AST containing crude oil and fuels have special requirements: they should be of light color (mostly white) in order to reflect sunlight and thus preventing the temperature rise of AST surface and fuels inside tanks, reducing evaporation and loss of fuels into the atmosphere; resistant to the atmosphere (industrial with polluted gases, marine with salts, etc.); to rains (sometimes accumulated on the AST roofs); to spillage of crude oil and fuels. The recommended thickness of these coatings in industrial atmosphere is over 250 μm (see Appendix L, Table L.3).

7.2.3 Coating Systems for Protection of Outer Surface of Underground and Submerged Pipelines

Underground and submerged pipelines for transportation crude oil and fuels are made from carbon steel and outer surfaces are protected by coatings and cathodic protection. Usually inner surface of these pipes is not protected. In rare cases inner surface of pipelines intended for transportation of jet fuel has special epoxy coatings. Coatings on the outside of pipelines transporting crude oil and fuels buried in the soil or in the water have the following requirements: resistance to groundwater (sometimes contaminated by fuels because of unseen leaks), to stones' hit (which may happen during installation), and compatibility with cathodic protection. The standard NACE SP0169-2007 [4] recommends using coal tar, wax, fusion bonded epoxy (FBE), polyolefin (polypropylene—PP and polyethylene—PE), polyurea, epoxy, and polyurethane coatings. One of the best coating systems is the three layer coating system consisting of the first layer FBE (thickness 450 μm), butyl adhesive layer, and outer layer of extruded polyolefin coating (thickness 1.5–3.0 mm, depending on pipe diameter) (see Sect. 5.7). FBE coatings have good adhesion to steel surface (as a result of presence of polar groups in epoxy), but like all epoxy coatings are fragile. Outer layer of polyolefin coating (which do not have enough adhesion to steel surface) is linked by butyl adhesive layer to FBE, is flexible and protects FBE against mechanical damage. Type of polyolefin (PE or PP) is chosen according to service temperature of pipelines. If temperature does not exceed 60 °C, PE may be chosen. If temperature is higher, for instance, about 90 °C for fuel oil pipelines, PP should be chosen. Usually three layer coating system is applied at the manufacture of pipes. Special procedure is developed for protection of welding zones in the field.

Pipelines for fuel transportation also may be made from fiberglass. It is important to emphasize that in practice different organic coatings (epoxy, polyurethane, polyurea, etc.) are used for the protection of outer surface of underground and submerged pipelines and they protect metals if they are applied correctly and maintained pore free but this is very difficult to do in practice. Therefore, in addition to these coatings it is necessary also to apply cathodic protection to outer surface of coated pipes (see Sect. 7.3). The role of cathodic protection is to protect areas with coating defects (scratches, pores, and holes). Organic coatings using for outer surface of underground and submerged pipes are dielectric materials with high electrical resistance ($R > 10^6 \Omega$). Therefore, electric current needed for cathodic protection of coated pipes is significantly lower than that of bared pipes.

7.2.4 Metallic Coatings

Metallic coatings using for protection of carbon steel systems for transportation and storage fuels are divided into *metal spraying*, *hot-dip* and *electrolytic coatings*. They differ by the way they are prepared.

Metal spraying is the process of producing metallic coatings on metal surfaces by means of spraying with compressed air of molten metals or alloys. Zinc, aluminum and their alloys may be used as *arc-sprayed* coatings for the protection of the inner and outer surfaces of the tanks from corrosion in fuels, atmosphere, and soil. This method also is called *flame spraying*, *thermal spraying*, *metalizing*, or *spray weld*. The metal used as a coating material may be wire or powder form. Molten particles of metal or alloys move with compressed air onto the metal surface to be protected, impact and flatten. Molten particles of metals are oxidized by the air during their moving from the “gun” to the metal surface. Therefore, a finished coating consists of a mixture of melted metal and its oxides which are solidified. The distance between the “gun” and the metal surface to be protected is usually about 1–2 m. The requirements for preparation of the metal surface are similar to those before painting. Metalizing equipment is mobile, appropriate for many complex shapes and not limited by size. Metalizing coatings of high porosity are formed. Porosity is the ratio of free volume (cavities) in the coating to the total geometric volume of the coating on a metal surface, which depends on the type of metal spraying (its density) and process type. Aluminum coatings have a higher porosity (5–15 %) than zinc coatings (1–3 %). The main drawback of high porosity is that corrosive components can penetrate through pores to the metal surface under a metalized coating. The minimum thickness of the coating is the thickness needed for closing of all the pores in the coating. Because of the different porosity of various metal spraying coatings, the minimum thickness needed for metal protection is also different. Thus, the minimum thickness for a zinc coating is 100 μm , for aluminum coating is 300 μm . The lifetime of metallic coatings depends on their thickness. Adhesion of metalized coatings is higher than that of paints. Zinc coatings are not resistant to H_2S if the latter is present in fuels, and the electrode polarity of zinc and iron may change during the cleaning of inner surfaces of tanks with hot water at 90 °C. This phenomenon can cause the dissolution of iron instead of zinc if cracks are present in the zinc coating. Aluminum coatings are resistant to H_2S and hot water, however, are susceptible to sparks, if a steel object falls inside fuel tanks containing flammable hydrocarbon gases. Therefore, the same requirements should be carried out during repair and maintenance work inside steel tanks with and without aluminum coatings. Zinc does not cause sparks in such cases. Zinc dust formed during the metalizing process is more dangerous for people’s health, than aluminum dust. Hot water treatment of aluminum coatings is favorable for decreasing their porosity because of the formation of aluminum hydroxides in the pores of the coatings. Besides the lack, porous surface possess by benefit that it is a good base for the penetration of liquid paints and the formation of combined metalizing–paint coatings on steel surfaces. The process of filling of the pores of metal spraying coatings with paint is called *sealing*. The approximate lifetime of aluminum-epoxy coatings in fuels is 30 years. Good adhesion of zinc and aluminum metalized coatings to steel allows the shaping of constructions (for example, sheets for tanks) in different forms without coating delamination. Aluminum and zinc coatings are used for protection inside and outside carbon steel surfaces of tanks. The advantage of metal sprayed coatings is that sheets with such coatings can be welded and then coated with arc-sprayed

and organic paints in field. Metalized coatings are rare in practice because initial cost is 50% higher than that of painting. However, after 25 years of service metalized coatings can save about 50%. Metalized coatings really are used for protection of small tanks (5–25 m³ volume).

Hot dip aluminized steel (called also *aluminized* or *aluminum-coated steel*) and *zinc-nickel galvanic coatings* also are recommended for tanks containing fuels with oxygenates. Canisters for purifying fuels are made from *aluminized steel* and *polyester* felt outer wrap. *Hot dip coating* is a process in which a protective coating is applied to a metal by immersing it in a molten bath of the coating metal (for aluminum, T_{melting} is 660°C). Hot dip coatings have following advantages: the ability to coat recessed or difficult areas (such as corners and edges) with a required coating thickness, resistance to mechanical damage (because the coating metallurgically bonded to a steel), and good resistance to corrosion in a number of environments.

Zinc-nickel galvanic coatings are coatings on steel which are produced by electrodepositing (electrochemical process) an adhering zinc-nickel alloy (7–15 wt% Ni) film on the surface of steel. This process also is called *electrogalvanizing* or *electroplating*. These coatings are not as thick as those produced by hot dip galvanizing and are mainly used as a base for paint.

Terne is an alloy coating (named also *terne coat*) that was historically made of lead (80 wt%) and tin (20 wt%) used to cover steel. Nowadays lead is replaced by zinc and this alloy consists from tin (50 wt%) and zinc (50 wt%).

7.2.5 Recommendations for the Selection Coating System

Durability and longevity of coatings depend on three stages: correct selection of the coating system for particular conditions of the tank (fuel type, geography, and atmosphere) or other constructions, surface preparation, and performance of coating. It is important the rigorous supervision of experts at each step, as well as to check the toxicity of all components of coating system that can damage to human health, safety, and deteriorate the environment. In fact, all coating systems (even solventless coatings composed of 100% solids) contain volatile substances which emit into the environment. Therefore, it is important to check the presence of volatile organic compounds (VOC) in paints. Special attention must be given to surface preparation [5].

7.2.6 Testing of Coating Compatibility Under the Conditions of Fuel Storage Tanks

In order to select correct coating system, it is important to carry out accelerated tests of resistance of coatings in aggressive model solutions under laboratory conditions [6–9]. The panels with tested coating systems are immersed in a three phase medium: 3% NaCl + 0.2% NaBO₃ aqueous solution, gasoline (or iso-octane) with 35% vol. toluene (or xylene) or 15% vol. MTBE added (the organic phase), and the

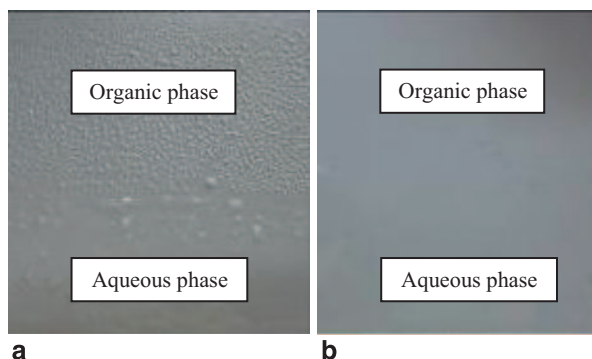


Fig. 7.1 PVC coating (thickness is 180 μm) after three months of immersion in: **a** aqueous solution (3% NaCl+0.2% NaBO₃), organic phase (65% vol. iso-octane+35% vol. xylene); blisters appeared on the coating in organic phase after a month of immersion. 2/3 of upper part of the panel was in organic phase and 1/3 was in aqueous phase. **b** aqueous solution (3% NaCl+0.2% NaBO₃), organic phase (85% vol. iso-octane+15% vol. MTBE); T=22 °C

vapor phase. The panels are placed in the beakers containing the aggressive model solution in such manner to enable examination of the resistance of the coatings in each of the three phases: aqueous, organic and vapor. Usually the temperature is 20–25 °C. In some cases gasoline may be changed on gas oil or fuel oil, and experiments are carried out at 90 °C. The tests at high temperature simulate the conditions in fuel oil tanks. Visual examination of coatings should be made every 7–10 days according to standards [10–12]. Such forms of deterioration of coatings as blistering, rusting, cracking, and peeling should be documented. The aggressive solutions must be refreshed every month. The experiments should be lasted not less than three months. As example panels with PVC coating after examination in two aggressive model solutions are shown in Fig. 7.1.

Adhesion of coatings to metal surface should be tested before immersion and after immersion of coated panels in aggressive model solutions [13]. *Adhesion is the pull-off strength between a coating film and metal surface needed for film removing.* Adhesion is defined as the greatest perpendicular force that a surface area can bear before a plug of material is detached. Therefore, adhesion is measured in values of pressure (psi) (Fig. 7.2).

Usually it decreases with an increase of the exposure time of coatings in the environment. Adhesion is one of the main coating properties defining the service life (duration) of the coating, and depending on the quality of the surface preparation, type of paint, coating thickness, and nature of a metal. Penetration of aggressive species through coating films from the environment to the metal surface depends on adhesion, and the latter, in its turn, depends on the penetrating properties (chemical resistance) of the coatings. The adhesion of coatings to steel must be larger 1,000 psi (pull-off test). Excellent adhesion is 2,000 psi and more.

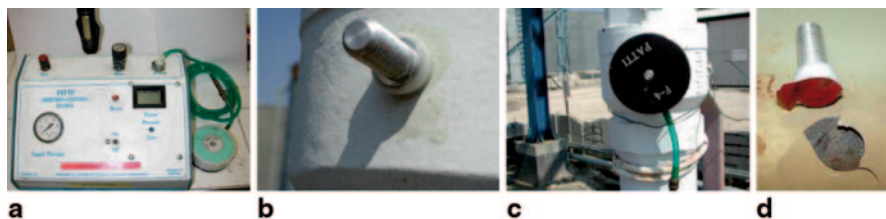


Fig. 7.2 **a** a device PATTI 2 for quantitative measuring of adhesion of coats to metals according to ASTM D4541 [13]; **b** an aluminum stub glued to measured coating; **c** measuring of adhesion of coating on the pipe; **d** a stub after measuring of adhesion (one can observe distortion of coating in the location between a metal and a primer—first coating layer)

It is important to examine the influence of selected coatings on the fuel quality (physico-chemical properties of fuels). We can choose and use coatings only after the period of its contact with fuel not less than a year and will not influence fuels' quality.

7.2.7 *Experience of Anti-corrosion Protection of AST*

Inner surface Usually only inner surfaces of bottoms and one meter of the height of the AST shells are coated. Each bottom contains many welds, patches, corners, and edges which are critical areas where breakdown of coatings can begin. They must be carefully cleaned and protected. Usually they have additional layer of coating (Fig. 7.3a). All critical areas should be given brush applied stripe coats with the same product as the consecutive system coat to achieve the minimum specified dry film thickness. The use of long handled brushes is not permitted.

Outer surface (Figs. 7.3b, c) According to ISO 12944-2 standard [14] the thickness of coatings in industrial atmosphere possessing very high corrosiveness (when corrosion rate of carbon steel is 0.1–0.2 mm/year) must be minimum 240 μm . Our experience forced us to increase this thickness to 300 μm . The cause is that coatings must be resistant to possible spillage of petroleum products and formation of immersion conditions in the case of use of flat or floating roofs. Sometimes coating systems using for anti-corrosion protection of AST in atmosphere consist of the first layer of inorganic zinc silicate coating, intermediate layer of epoxy coating and outer layer of polyurethane coating of white color which has high reflecting properties (Appendix L, Table L.3). Epoxy coatings do not resist to atmosphere because of chalking. Therefore, polyurethane coating should be used as outer coating in contact with atmosphere. Our experience showed that it is possible using the surface tolerant aluminum mastic epoxy or epoxy primer as the first layer instead of inorganic zinc silicate coating. The latter coating must be used only when surface preparation is carried out carefully according to Sa 2.5 [15]. The surface tolerant aluminum mastic epoxy coating can be used when surface preparation is not so

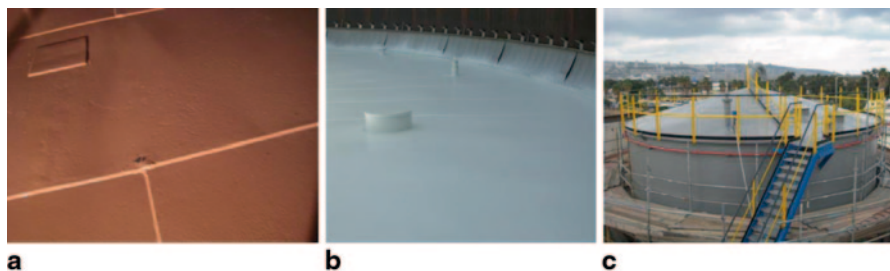


Fig. 7.3 **a** Inner surface of the bottom coated by epoxy novolac. Average thickness is 570 μm (minimum 550 μm). Welds and patches are well coated (have additional thickness). AST is intended for storage of kerosene. **b** Outer surface of the floating roof with coating system: surface tolerant aluminum mastic epoxy (125 μm) + surface tolerant mastic epoxy (125 μm) + polyurethane (50 μm). Minimum thickness is 300 μm . AST is intended for the storage of gasoline. Outer surface contacts the atmosphere at the oil refinery and sometimes spillage of gasoline. **c** The 1st layer—epoxy primer (100 μm); the 2nd layer—epoxy high build (100 μm); the 3rd layer—polyurethane (50 μm). Total—250 μm

good (St 2 according to [15]), old paint and dense rust are remained on the surface (Appendix L, notes to Table L.3).

7.3 Cathodic Protection

The electrochemical mechanism of corrosion in electrolytes allows the use of electric current and electric potential in order to protect metals from corrosion. Therefore, electrochemical methods work only in solutions of electrolytes and can not work in fuels and other non-conductive media. When a pipe made from carbon steel without coating is in the soil a pipe corrodes according to electrochemical mechanism (see Sect. 5.1). Carbon steel pipe is an anode that corrodes.



Cathode does not corrode. Thus if we turn this pipe from an anode to cathode it will not corrode. We can reach this if we connect iron to a metal possessing by lower electric potential, for example, zinc, aluminum, magnesium or their alloys. The metal which has a lower electric potential will be anode, will corrode and will protect iron in a solution of electrolyte (wet soil or seawater).

Thus iron will serve as cathode and will not corrode. This is an example of ‘beneficial’ galvanic corrosion and the principle of *cathodic protection* (CP). We meet in this case the constructive role of corrosion. Anode (zinc, aluminum or magnesium) corrodes and protects a cathode (iron) from corrosion. Zinc, aluminum and magnesium are called *sacrificial anodes*, sometimes anodes of *galvanic type*.

Another way to suppress the anodic dissolution (Eq. 7.1) is to change the direction of this reaction from right to left. Thus, if we connect the iron to the negative

pole of a direct current power supply, electrons will move to the iron, and reaction (Eq. 7.1) in right direction would slow down to a negligible value or even to stop it. In *cathodic protection* (CP), metallic equipment is connected to a *metal* with a lower electrical potential or to *negative* pole of power supply and turns completely into a cathode, which does not corrode. This method is realized for protection of inner surface of bottoms of AST containing crude oil in the presence of aqueous solution at the bottom, outer surface of bottoms of AST in contact with soil or sand, outer surface of UST shell containing fuels, and outer surface of underground and submerged pipelines for transportation crude oil and fuels. Outer surface of bottoms of AST may contact concrete, sand, or soil. When we are talking about CP of outer surfaces of metallic tanks and pipelines there is no matter what kind of fuel is inside. CP can be applied for systems for storage and transportation of fuel oil and asphalt when temperature may reach 100–175 °C. Different standards exist for implementation of CP of the outer surface of AST bottoms [16–20]. Elevated temperatures, disbonded coatings, shielding, microbiological attack, areas of the tank bottom that do not come into contact with the electrolyte, and dry tank cushion are the conditions in which CP is ineffective or only partially effective.

7.3.1 Internal Cathodic Protection

It is impossible to use CP inside AST containing fuels because the latter are not electrolytes. Water accumulated at the bottom of kerosene and gas oil tanks usually is drained. Zinc and magnesium sacrificial anodes can be used on the tank bottoms containing crude oil if aqueous phase (with salt content >0.3 wt%) is also present on the bottom. The selection of the anode material depends on the electric conductivity of aqueous phase. If electric conductivity is low, magnesium anodes can be used. Usually zinc anodes are used inside. They are welded to the bottom material inside of crude oil AST. Aluminum anodes are not recommended to use inside because they can cause a spark in the presence of flammable gases (light hydrocarbons).

7.3.2 Cathodic Protection of the External Surface of AST Bottoms, UST, Underground and Submerged Pipelines

Sacrificial anodes or impressed current are used to protect the outer surface of AST bottoms and UST irrespective to type of fuel stored in them [17–24]. Impressed current is used for the CP of the external surface of the bottoms of tanks containing hot asphalt to 175 °C [24–26]. Sacrificial anodes also are used for protection of the secondary containment and double floor [27] (see Sect. 7.8). Usually anodes are distributed around the tank, or installed under the bottom before its erection, or put at the depth of 60–100 m [22, 23]. It is very important to choose the reference electrode for measuring the electrode potentials of bottoms protected at high temperatures. This method is used for new tanks and tanks that are already in service.

Different standards and specifications determine the installation and use of cathodic protection systems, including testing methods and monitoring its effectiveness [4, 19–21, 28–33]. CP of the external surface of the bottoms of tanks allows reducing the corrosion rate nearly to zero [34]. UST external surface should be protected in accordance with the standard [20]: coatings + cathodic protection. The type of these coatings is identical to that used for external surface of underground pipelines (see Sect. 7.2.3). CP does not work on inner surface of pipelines containing fuels. It protects only outer surface of fuel pipelines. It is important to emphasize that CP must be used on external surfaces of coated UST, underground and submerged pipelines. However, not always CP must be applied on external surfaces of AST bottoms. When bottoms are installed on sand mixed with asphalt (bitumen) or on concrete basement there is not necessary to use CP.

CP does not work on underground constructions with thermal isolation [35]. Only use of special coatings under the thermal insulation can prevent the development of corrosion under insulation (see Sect. 5.9 and Appendix L, Table L.4).

7.4 Corrosion Inhibitors

Corrosion inhibitors are chemicals that, when present in low concentrations (1–15,000 ppm) in a corrosive environment, retard the corrosion of metals. Corrosion inhibitors are spent in electrochemical corrosion reactions. They can be solids, liquids, and gases, and can be used in a solid, liquid, and gaseous media. We will describe corrosion inhibitors and their use in liquid and vapor phase of fuels.

7.4.1 Liquid Phase

Addition of corrosion inhibitors to fuels and biofuels plays an important role in corrosion control. Examples are the addition of water for prevention general and pitting corrosion of aluminum in methanol and ethanol; injection of carboxylates, long-chain amines, sulphonates, and naphthenates for prevention of carbon steel corrosion in fuels. Many corrosion inhibitors, such as amines, amides, acetates, and sulphonates, dissolved in the hydrocarbon phase, are known but they have not found wide use in fuels. Small quantities of water in fuels (200–1,000 ppm) can cause severe corrosion of carbon steel. Inorganic corrosion inhibitors (nitrite NaNO_2 and phosphates Na_3PO_4 , Na_2HPO_4) injected in concentrations of 200 ppm and more to mixtures of gasoline and water effectively protect carbon steel from corrosion even during stagnation, that is under conditions existing at the bottoms of tanks (Fig. 7.4; [36, 37]).

In any case corrosion inhibitors are more effective under agitating conditions. Therefore, they may be injected into gasoline pipelines but they will work only in the presence of water. Inorganic corrosion inhibitors are dissolved in aqueous phase and are not dissolved in organic phase.

Fig. 7.4 Carbon steel coupons after immersion in two phase system gasoline–water with different concentrations of NaNO_2 . Seven days; 25°C ; agitation. Reference is original coupon

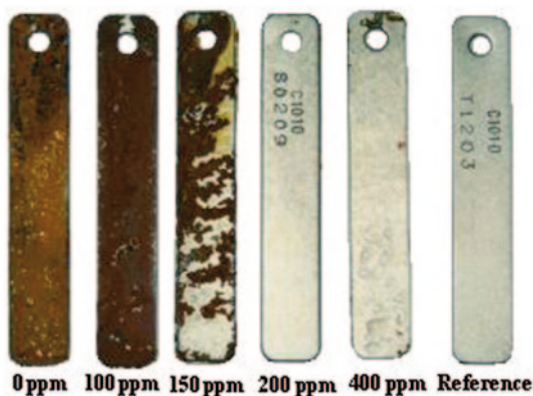
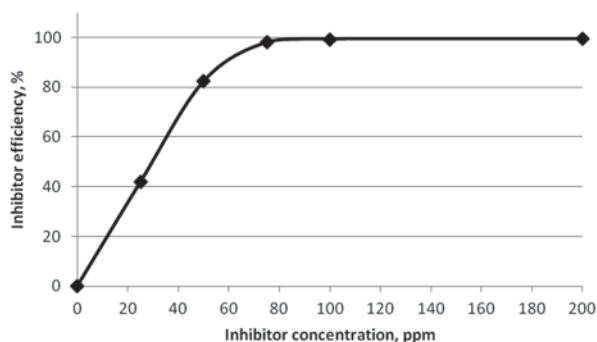


Fig. 7.5 Efficiency of inhibitor Na-SUL-EDS in two-phase system gasoline + 1% vol. H_2O (containing 100 ppm NaCl)



Organic inhibitor Na-SUL-EDS (sodium ethylenediamine dinonylnaphthalene sulfonate) in concentrations >100 ppm is recommended for protection of carbon steel in gasoline at $25\text{--}40^\circ\text{C}$ (Fig. 7.5 and Table 7.2). We should emphasize that minimum critical concentration of 100 ppm exists because pits are formed on carbon steel surface at concentrations below this value (see Fig. 7.6).

We have to take into account the environmental requirements regarding the possible leaks and drainage water with corrosion inhibitors.

7.4.2 Vapor Phase

In my childhood, winter clothes were stored in a wardrobe for summer. My mother put white tablets of naphthalene into these clothes against moth. Every time when I opened the wardrobe I felt a pungent odor of naphthalene. This meant that naphthalene molecules were transformed directly from solid to vapor phase. Then I went to the university and learned that pure substances may be changed from a solid to a vapor phase under certain conditions (at suitable pressure and temperature).

Table 7.2 Corrosion rate of carbon steel in two-phase system gasoline + 1 % vol. H₂O (containing 100 ppm NaCl) at different concentrations of inhibitor Na-SUL-EDS

Inhibitor Concentration, ppm	Corrosion Rate, mm/year	Inhibitor Efficiency, %
0	1.085	0
25	0.631	41.8
50	0.192	82.3
75	0.022	98.0
100	0.007	99.3
200	0.006	99.4
400	0.004	99.7
500	0.006	99.5
1,000	0.007	99.4
5,000	0.010	99.1
10,000	0.002	99.8
15,000	0.005	99.5

Carbon steel coupons were immersed at agitation at 25 °C for 6 days. Concentrations 1,000–15,000 ppm were recommended by the manufacture of the inhibitor Na-SUL-EDS. Inhibitor

efficiency (E , %) was calculated according to: $E, \% = \frac{CR_0 - CR_i}{CR_0} \cdot 100\%$

CR_0 the corrosion rate of carbon steel in gasoline-electrolyte mixture without inhibitor;

CR_i the corrosion rate of carbon steel in gasoline-electrolyte mixture with inhibitor of different concentrations.

We are familiar with some solid substances (naphthalene, iodine, “dry ice”—CO₂) which are transformed into the gaseous phase, passing the liquid phase, at atmospheric pressure and ambient temperature. This process is called *sublimation*. Different solid organic substances possess by inhibitor properties and sublimate under environmental conditions. They are dicyclohexylamine nitrite (NDA), cyclohexylamine carbonate, some amines and imines, diisopropylamine nitrite, ammonium nitro benzoate, salts of nitrobenzoates and benzoates [38–44]. These substances are used for the protection of the inner surface of the upper parts of AST that contact the gaseous phase containing hydrocarbon and water vapors, air, and H₂S emitted from the liquid fuels. These organic substances are called *vapor* (or *volatile*) *phase inhibitors* (VPIs) or *vapor corrosion inhibitors* (VCI). The theory and mechanism of protective properties of VPIs is developed well. When the solid VPI is present inside of the AST above the liquid fuel, the molecules of VPI sublimate from solid to vapor phase and diffuse under the roof into all places including corners, cracks, and crevices. When the VPI molecules reach metallic surface they are adsorbed and form mono- or poly-molecular layers on this surface protecting it from ‘sheltered’ atmospheric corrosion by H₂O, O₂, H₂S, CO₂, SO₂, and SO₃ under the roof in the AST. Therefore, they also are called *inhibitors of atmospheric corrosion*. The mechanism

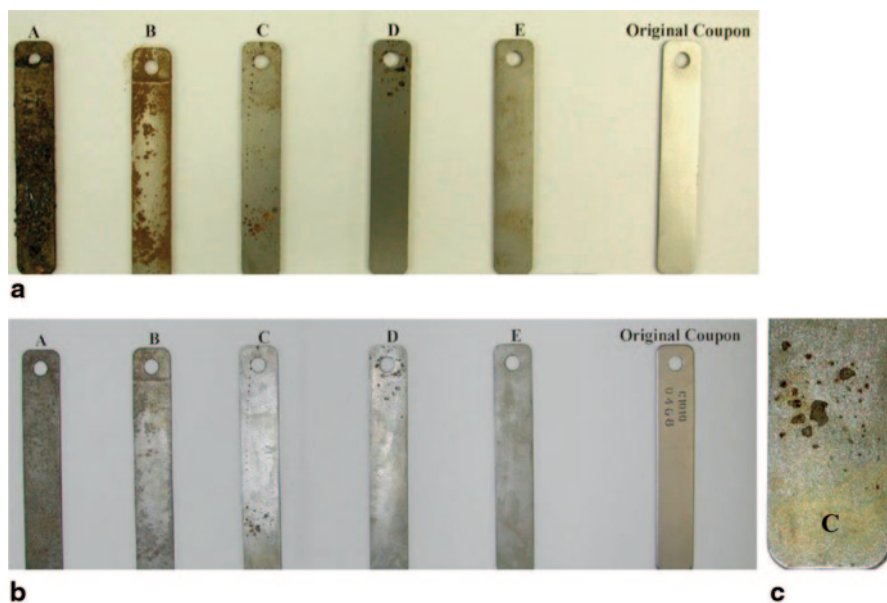


Fig. 7.6 Carbon steel coupons after experiment in two-phase system gasoline + 1% vol. H_2O (containing 100 ppm NaCl) at different concentrations of corrosion inhibitor Na-SUL-EDS before (a) and after (b) chemical cleaning. **c** Magnification of the coupon C. Agitation at 40 °C for 6 days. A 25; B 50; C 75; D 100; E 125 ppm corrosion inhibitor. One can see pits on coupons A, B, C

of this corrosion is an electrochemical in thin layer of electrolyte. A unique feature of VPIs is that their partial pressure is relatively large at ambient temperature, and as a result there is a high capacity to penetrate into crevices. VPIs may be used as solids (granules, tablets, powder) or in liquid solutions. Some of these organic molecules (e.g., NDA) are toxic substances. Biodegradable VPIs were developed [45]. Some VPI compounds protect only ferrous alloys; others protect both ferrous and non-ferrous alloys. Usually VPIs protect pure steel surface (free from rust) but sometimes it is possible to stop corrosion of rusted steel. The efficiency of VPIs depends on their vapor pressure, the airtightness (hermeticity) of the AST, temperature, and water vapor content (relative humidity) in gaseous phase under the roof. It is impossible to close an AST tightly from the atmosphere because of the “breathing” process a tank undergoes. As a result of the “breathing”, vapors are emitted from the tanks during filling, and air with water vapor enters during emptying of the tanks. VPIs can be used alone or in combination with dryers of water vapor (desiccants) like silica gel or zeolite. A VPI must be injected in the vapor zone of the tanks throughout their service. The VCI diffuser is developed which can be mounted on the outer surface of the roof AST [46, 47]. Inhibitor is injected through the diffuser in order to maintain required its vapor pressure (and as a result its concentration) in the top (above liquid fuel) of the AST. VPIs can reduce the corrosion rate of carbon steel roof to ten and more times, and allow extending the life of the roofs of AST up to 30 and more years.

7.5 Anti-Bacterial Treatment

Fuels can be deteriorated by microorganisms in as little as 6 months. To inhibit or prevent the bacterial deterioration of fuels and MIC in fuel systems, anti-bacterial treatment is needed (see Sects. 2 and 5.4). Kerosene (jet fuel), gas oil (diesel fuel) and crude oil are mostly needed this treatment. For this, biocides in concentrations 10–300 ppm are injected depending on the type of biocide, fuel and the aim (for instance, for sterilization or maintain fungi free fuel). Biocides are toxic substances for microorganisms. Isothiazolone, isothiazolin, quaternary ammonium compounds, organoborinanes, pyridinethione, hexahydrotriazines, imidazolcarbamate and others are used. A biocide may not work if a thick biofilm has formed on the surface of the tank or other equipment, because then it does not reach the organisms living deep within the biofilm. In such cases, the tank must be drained and mechanically cleaned. Even if the biocide effectively stops microbial growth, it still may be necessary to remove the accumulated biomass (the dead microorganisms) to avoid filter plugging and they may be nutrients for living microorganisms. It is possible to use enzymes that catalyse the disruption of the microorganisms into particles that can be filtered out or burned up with the fuel.

The best method of controlling microbial sludge formation is through periodical drainage (once a week) of water and periodical microbiological control of water and fuel phases. The important parameter of the total bacteria count (TBC) is its growth tendency rather than its absolute value. If $TBC = 10^3$ bacteria/ml in the aqueous phase, and this TBC value is constant with time (it is recommended checking once a month), and $TBC = 0$ in the fuel, the latter is not contaminated by microorganisms. The pH of aqueous phase in this case may be 5–7. Any changes of conditions can result in a sudden proliferation of microorganisms and deterioration of fuels.

Any water bottoms that contain biocides must be diluted and deactivated prior to discharge or disposed appropriately. For instance, isothiazolines are readily degraded to nontoxic components by the addition of slightly acidic 10% solutions of sodium metabisulphite ($Na_2S_2O_5$) or sodium bisulphite ($NaHSO_3$). We should be sure that after the anti-bacterial treatment of fuels remains of biocides in aqueous phase are deactivated (destroyed). Otherwise, they can kill “useful” microbes functioning at the biological treatment of the wastewater plant.

7.6 Technological Measures

Technological methods include:

- Drainage of water and periodic cleaning of AST bottoms and inner surfaces of pipelines from sediments.
- Maximum filling of tank space with fuel (the level of fuel must be as higher as possible).

- The storage of fuels under the pressure of inert gas (nitrogen) which must not contain water vapor and oxygen.
- Drying air which enters the tanks through vents. The relative humidity of entering air should be less than 40% in order to maintain low corrosion of inner surfaces of tanks.
- Treatment of fuels. Injection of scavengers of hydrogen sulphide and oxygen facilitates removing these two dissolved gases from fuels.
- Use of coalescers helps to remove water from fuels.

Regulations in some countries [48] recommend using prevention measures, such as elevating tanks, resting tanks on continuous concrete slabs, installing double-walled tanks, internally lining tanks, cathodically protecting the tanks, and inspecting tanks according to API standards [49].

Correct installation of AST on sand mixed with bitumen may prevent corrosion of outer surfaces of the bottoms. The inspection by the author of outer bottom surfaces of the AST in contact with oily sand after 60–80 years of service in some regions in Israel and South Russia supports this rule.

7.7 Combined Methods of Corrosion Control

Different anti-corrosion protection methods can be used in combination. For example, coatings together with cathodic protection or water-soluble corrosion inhibitors can be injected where sacrificial anodes are installed for the protection of the inner surfaces of the crude oil storage tank bottoms [43, 47, 50–52]. Synergistic effect allows reducing the concentration of inhibitors 3–6 times and the electric current of cathodic protection 2–5 times. Inorganic inhibitors (NaNO_2 , Na_2HPO_4 , ZnSO_4 , ZnMoO_4) or organic ($\text{C}_{13}\text{H}_{26}\text{NO}_2$, $\text{C}_{11}\text{H}_{28}\text{N}_3(\text{PO}_3)_3$, $\text{C}_2\text{H}_9\text{SNO}_4$, $\text{C}_{17}\text{H}_{30}\text{NCl}$) at concentrations of about 30 ppm and zinc sacrificial anodes are used for this purpose. Important condition is the presence of an electrolyte solution at the bottom of tanks. Usually such conditions are keeping in crude oil AST. It is necessary to take into consideration the requirements of preservation of the environment and to select environmentally friendly corrosion inhibitors. Use of coatings also allows significantly decreasing electric current needed for cathodic protection.

All anti-corrosive techniques described in this section are compatible also for the protection of the inner surfaces of underground storage tanks.

7.8 Secondary Containment and Double Bottom

In order to avoid unexpected leakages of fuels, new and old tanks after renovation are installed with secondary containment or double bottom (double containment) [53–56]. The principle of the double bottom is to install the new carbon steel bottom

above the old rusted bottom that is to remain it and not to concern. Usually the space between the two bottoms (old and new) is filled with dry “sweet” sand which does not contain salts. Drainage system is installed in this space and is intended for detection leakage of fuel in the case of corrosion and formation of holes in new bottom. The sand is dry and inert towards the new bottom at the beginning of its use. However, with time during “breathing” the level of the fuel in the tank changes (up and down) and according to these changes air with water vapor can enter into the space between the two bottoms through the drainage system. Thus corrosion can develop over time and cause the formation of holes in new bottom and leaks of fuel. In this case, cathodic protection (impressed current) of outer surface of new bottom is used with control its efficacy [28, 57–61]. Concentric circular ribbons bed anodes are installed in the space underneath tank bottom (outer surface of new bottom and dielectric secondary containment barrier made of HDPE of 2 mm thickness). When fuel oil or asphalt is stored in tanks the temperature can reach 150 °C. In this case HDPE secondary containment liner is installed at the depth of one meter underneath the tank bottom in order to decrease possible deterioration of the polyethylene due to high temperature.

7.9 Underground Storage Tanks

Underground storage tanks (UST) containing fuels are of paramount importance because usually they are installed in populated areas (e.g., gas stations in cities). Therefore corrosion protection of UST is very important. Construction and installation of UST is defined by standards [20, 62, 63]. Three types of carbon steel UST are recommended for use: with sacrificial anodes installed by the manufacturer of tank; coated with fiberglass (fiberglass clad); and with HDPE jacketed. According to the specification of Steel Tank Institute (USA), UST can be produced with three level of corrosion control: coating of external surface; installation of nylon bushings which isolate the tank from the pipes entering and connecting to the tank; and installation of sacrificial anodes at the factory (by the manufacture of UST). Sacrificial anodes are installed on the surface of coated tanks in order to protect possible scratches of coatings which can happen during transportation and mounting UST in soil. Flexible piping, running from the tank to the dispenser, are made of HDPE lined with Nylon or PK (polyketone) for permeation and swelling resistance to fuels.

The use of UST with double walls and installation of sensors for the detection of fuel leakage are defined by standards [20, 62, 64]. UST made from fiberglass also are permitted for use [20, 64]. By the mid-1960’s fiberglass was accepted for the storage and handling of underground flammable and combustible liquids. Since an UST made from fiberglass is buried, it is subjected to combined compressive loads from the soil, the water table and the live loading. To resist global buckling, composite UST’s are equipped with circumferential stiffening rings.

Fiberglass UST also are used for the storage of MTBE and alcohol-gasoline blends. Older fiberglass UST, installed before 1979 are more prone to absorption

of alcohols than newer tanks designed for E10 service. In older tanks, flexural stiffness retention was estimated to be 70 % after 30 years exposure to E10 blends while methanol blends retained only 25 % stiffness. Newer tanks, listed for ethanol service retain properties considerably better. The storage of alcohol-gasoline blends may lead to an increased frequency of buckling failures in tanks that were not designed to store these fuels.

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Chapter 8

Corrosion Monitoring and Nondestructive Testing in Systems Containing Fuels

All our knowledge begins from sensations

Leonardo da Vinci (1452–1519), the Italian polymath

Abstract Corrosion monitoring methods are the control methods of corrosion situation. Nondestructive Testing (NDT) is a wide group of analysis techniques used in industry for evaluation the properties of materials without causing damage. Visual examination, ultrasonic testing (UT), eddy current and their modifications, acoustic emission (AE), radiography, infrared thermography, penetrant testing, magnetic and electromagnetic methods as NDT techniques using in systems containing fuels are described. On-site chemical analysis of alloys also is described. Weight Loss (WL) and electrical resistance (ER) methods are analysed. Examination and control of the environment include chemical analytical, physico-chemical, physical, and microbiological analysis of media (crude oil, fuels, water, two-phase solution, gaseous phase, and soil) which contact surface of tanks and pipes. Control of the interphase metal–environment is based on its physico-chemical properties and includes electrochemical methods, identification of corrosion products and deposits, and examination of the morphology of the metal surface.

On-line real-time corrosion monitoring methods including cathodic protection efficiency that found wide use for corrosion monitoring in systems containing fuels also are described. Maximum recommended intervals between inspections of tanks containing different fuels are given. Standards for corrosion monitoring and testing are recommended. Rich bibliography is given on each topic.

People from the ancient times used nondestructive testing (NDT) for detection different defects in materials (including corrosion phenomena and their consequences). In order to realize that, people used their organs of sense: *sight*, *hearing*, *touch*, *smell*, and *taste*. We can detect corrosion damages on metals and coatings, such as rust, pits, and cracks by visual examination, and corrosion products according to their color. An engineer is listening to a working pump in order to define a cavitation—a specific noise similar to the sounds which we hear during the movement of stones. Smell of different substances (e.g., gasoline, hydrogen sulphide, mercaptans, ammonia, etc.) in the environment can show their leakage as a result of corrosion holes. We can define the presence of biofouling at a metal surface according to

the specific slippery feel of slime. The black color of biofilm points out the presence of SRB.

There is no corrosion preventive method that allows fully (100%) protect tanks and pipelines from corrosion. Corrosion monitoring (CM) methods and NDT using for tanks, pipelines, and other equipment containing fuels are described in this section.

Corrosion monitoring methods are the control methods of corrosion situation, namely, control of metal behavior under particular environmental conditions. Non-destructive Testing (NDT), also named Nondestructive Examination (NDE), or Nondestructive Evaluation (NDE) or Nondestructive Inspection (NDI) techniques is a wide group of analysis techniques used in industry for evaluation the properties of materials without causing damage. The term NDT encompasses *visual examination, ultrasonic testing (UT), eddy current, acoustic emission (AE), radiography, infrared thermography, penetrant testing, and magnetic flux.* All these methods are based on physical phenomena (*electromagnetic radiation or sound*) taking place inside a metal or on its surface. Some NDT, for instance UT, need preliminary surface preparation for measurements. Spectroscopic chemical analysis of alloys is related to NDT. Physico-chemical methods such as Scanning Electron Microscopy and Energy Dispersive Energy, Scanning Tunneling Microscopy, Atomic Force Microscopy using for the assessment of corrosion surface, corrosion products, bio-deterioration and micro characterization of different materials, are also NDT. *The goal of both NDT and CM is to give an indicator of the potential for degradation of structures and the equipment before significant damage occurs and to allow reducing the rate of degradation to an acceptable level.* NDT and CM are very versatile and developing interdisciplinary topics which found wide application for assessment corrosion in systems containing fuels. The properties of a metal, of an environment, and of an interphase metal–environment are used for CM.

Control of a metal condition is based on its physical properties: mass, thickness, and electrical resistance of the metal sample. Control of the environment is based on the chemical, physico-chemical and microbiological properties, and conditions of the environment. Control of the interphase metal–environment is based on the detection of physico-chemical properties of the interphase.

8.1 Control of Physical Properties of a Metal

Historically physical methods were the first: man's eyes (sometimes with magnification glass). Now in addition to eyes, optical devices (video cameras, microscope, stereo video microscope, and borescope) are used for visual control of properties of corroded metal surface. Visual methods are possible in most cases during shutdown. Bell-hole excavations are carried out for evaluating of corrosion on external surfaces of pipelines and UST. Video cameras are used for inspection of inner surfaces (including coating assessment) of tanks and pipes. A borescope is a general name of an optical device consisting of a rigid or flexible tube with an eyepiece on one end,

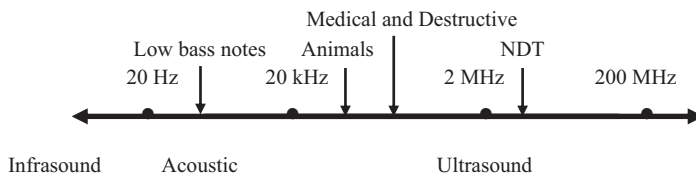


Fig. 8.1 Ultrasound range diagram

an objective lens on the other linked together by a relay optical system in between. Rigid or flexible borescopes may be fitted with a video or charge-coupled device camera. Sometimes borescopes are divided into fiberscopes (flexible borescopes), videoscopes (video borescopes), and rigid borescopes. Criteria for selecting a borescope are usually image clarity and access. Remote visual inspection is used for real-time views and images from inside of pipes, tanks and any enclosed structures. Optical microscope and profilometry are used for analyzing and measuring of pits' depths. Optical imaging techniques eliminates the influences of human subjectivity by digitally capturing the sample images under enhanced illumination conditions and then subjecting them to image analysis managed by computer software.

Different devices based on physical phenomena, allow to measure the changes in thickness of tanks and pipes containing crude oil and fuels: UT, AE, eddy current, magnetic flux leakage, and X-ray radiographic methods.

8.1.1 Ultrasonic Technique (UT)

What is ultrasonics? Like the visible spectrum, the audio spectrum corresponds to the standard human receptor response function and covers frequencies from 20 Hz to 20 kHz. For both light and sound, the 'human band' is only a tiny slice of the total available bandwidth. Ultrasonics is defined as that band above 20 kHz. In other words, ultrasound is a cyclic sound pressure with a frequency greater than the upper limit of average human hearing. Approximate frequency ranges corresponding to ultrasound, with rough guide of some applications are shown in Fig. 8.1. Two regions, acoustic and ultrasound, are used for NDT.

UT is a type of NDT commonly used to find flaws in materials and to measure the thickness of objects and thus, to monitor corrosion. Frequencies of 2–50 MHz are commonly used. Ultrasonic waves travel slowly, about 100,000 times slower than electromagnetic waves. This provides a way to display information in time. Ultrasonic waves can easily penetrate opaque materials, whereas many other types of radiation such as visible light cannot. Since ultrasonic wave sources are inexpensive, sensitive, and reliable, this provides a highly desirable way to probe and image the interior of opaque objects [1].

UT uses high frequency sound waves transmitted through the metal. The sound is reflected from other surfaces (the opposite metallic wall, anomalies in metal). The

time taken for the sound to transverse the thickness of metal and return to the probe is displayed as a metal thickness. UT devices are portable or fixed, and measure thicknesses from 1 to 300 mm to an accuracy 0.1 mm, sometimes to 1 % of the wall thickness. Usually the maximum temperature for the solid coupled probes in UT is 250 °C, but in some cases 500 °C can be reached [2].

Ultrasonic waves in solids can roughly be divided into two groups, the bulk waves and guided waves. The majority of ultrasonic testing are carried out with bulk waves. In this case, the wavelength of the waves is small compared to the dimensions of the object under inspection. Relatively localized information is obtained with this type of waves. This disadvantage is overcome by using of guided waves which allow obtaining wall thickness map. Guided waves, named also Guided Lamb Waves in honor of the English mathematician Horace Lamb (1849–1934), who analysed and described acoustic waves of this type in 1917, are elastic waves whose particle motion lies in the plane defined by the plate normal and the direction of wave propagation. In this case, the wavelength is typically in the order of wall thickness or even larger. The guided waves may propagate over very long distances and hence may provide global information. A variety of guided wave modes exists in plates and pipes, and majority of these wave modes are dispersive. This means that their phase velocity depends on the frequency and wall thickness. This property is used for instantaneous monitoring of the wall thickness of plates and pipes. This method is capable for determining the wall thickness of large areas with only a limited number of ultrasonic transducers. The wall thickness is determined between two transducer arrays. These transducers excite specific guided wave modes that are highly dispersive. Ultrasonic Guided Lamb Wave Tomography is based on propagation and measuring Guided Lamb Waves in metals and is used for instantaneous CM of fuel storage tanks, pressure vessels, and pipelines [3–6]. Non-contact electromagnetic acoustic transducers (EMAT) in thin metal plates also are widely used [7].

Ultrasonic thickness measuring instruments usually are the most accurate means for obtaining thicknesses on pipes with diameter larger than 33 mm. When corrosion is nonuniform, UT is not effective. In this case, radiography, ultrasonic scanning and eddy current devices are used. Radiographic profile techniques are preferred for pipe diameters of 33 mm and smaller.

Two types of ultrasonic sensors for on-line wall thickness monitoring are developed: low temperature (–40 up to 120 °C) and high temperature (up to 350/500 °C) [2]. These sensors are intrinsically safe, simply bond or are clamped onto the inspection area (usually at selected critical points), and thus allow receiving on-line corrosion data excluding erecting scaffoldings, removing insulation, shutdown plants, eliminating excavation and thus decrease inspection cost. These sensors can measure the metal thicknesses of 3–19 mm; suitable for pipe diameters of 3" up to 30", and even more.

Traditional manual UT has disadvantages: often UT measurements do not show localized corrosion, very large number of points measuring (several ten thousands) is required, and time consuming.

Automated ultrasonic scanners (crawlers) are used to rapidly inspect the thickness of large metallic structures at small measurement intervals, providing a high

detailed thickness map of the scanned surface (tank floors, shells and roofs, vessels, and pipes). Scan velocities are over 0.5 m/s. Most of the data in oil refineries' units is received from ultrasonic measurements carried out on shutdown (every 4–5 years) basis.

Phased array ultrasonic technology is an advanced method of UT [8–10]. Manual UT is much better at detecting planar discontinuities, but the results are dependent on the operator. Automated UT typically involves large, expensive and inflexible systems, though the results are reproducible. Portable phased array UT equipment is highly computerized fast method and can be operated in manual, semi automated or fully automated modes. Impossibility to detect localized corrosion which is inherent to UT is overcome by acoustic emission.

8.1.2 Acoustic Emission (AE)

One is familiar with the sound of breaking glass, plate or ceramic statue, falling tree and cracking ice. Even if we do not see breaking vase we understand what happens according to the sound that we hear. A “*tin cry*” is the characteristic sound heard when a bar of tin is bent. This “screaming” or “crackling” sound is caused by the shearing of crystals in the metal. Niobium, indium and gallium exhibit a similar effect.

AE is a phenomenon of sound and ultrasound wave generation (see Fig. 8.1) *by materials that undergo deformation and fracture* [11]. AE is the generation of transient elastic waves during the rapid release of energy from sources within a material caused by the changes in the internal structure [12]. When a structure is subjected to an external stimulus (change in pressure, load, or temperature), localized sources trigger the release of energy, in the form of stress waves, which propagate to the surface and are recorded by sensors. With the right equipment and setup, motions on the order of picometers (10^{-12} m) can be identified. Sources of AE range from natural events like earthquakes to the initiation and growth of cracks, dislocation movements, phase transformations in metals, and fiber breakage in composites. Most of the sources of AEs are damage-related; thus, the detection and monitoring of these emissions are commonly used to predict material failure. AE is unlike most other NDT in two regards. The first difference pertains to the origin of the signal. Instead of supplying energy to the object under examination, AE technique simply listens for the energy released by the object. AE tests are often performed on structures while in operation, as this provides adequate loading for propagating defects and triggering acoustic emissions. The second difference is that AE technique deals with dynamic processes, or changes, in a material. This is particularly meaningful because only active features (e.g., crack or pit growth) are highlighted. Sources generating AE in different materials are unique. In metals, primary macroscopic sources are crack jumps, processes related to plastic deformation, fracturing and de-bonding of inclusions. On the microscopic level, as plastic deformation occurs, ionic planes slip past each other through the movement of dislocations. These atomic-scale deformations release energy in the form of elastic waves which “can be thought of

as naturally generated ultrasound” traveling through the object. Leaks, frictions, knocks and chemical reactions belong to secondary class of AE. Quantitative and qualitative characteristics of AE waves, generated by sources of different nature depend on material properties and environmental factors. Both sources are related to corrosion phenomena. Corrosion reactions generate elastic waves (sounds) which may be detected by sufficiently sensitive instrumentation to provide an identifiable acoustic signature. Electrochemical corrosion reactions (anodic and cathodic) are accompanied by the radiation of signals having a low amplitude; the destruction of oxide films on the metal’s surface followed by localized corrosion (pitting, crevice, erosion, cavitation, SCC) produces AE of an explosive type with relatively small amplitude. Penetration of water, gases, and ions through the coatings can result in their disbondment, blisters and rupture, which are AE sources. AE provides a NDT for detection localized corrosion of different structures and equipment: LPG pressure tanks, AST, UST, piping systems, corrosion under thermal insulation, detection of flaw initiation and failure of coatings on metallic surfaces [13–21]. This method need not to empty or clean the tank. AE method allows inspecting one tank of diameter of 50 m during 8 h. Highly sensitive AE sensors are attached to the outside of the tank wall (up to 170°C) and the tank monitored, following a period of conditioning during which valves are closed and heaters/agitators turned off. The coupling of AE and thermogravimetric techniques are used for high temperature degradation and receiving information of the growth of the scales and mechanical stresses of alloys in oil refining and petrochemical industries [22].

The advantages of AE technique are: a non-invasive method and does not require an external source of energy (as do UT); in-service on-line real-time monitoring for corrosion behavior of metals, polymeric, ceramic and composite materials, fast diagnosis; it does not require access to the whole examination area; it is the only NDT that can detect early and rapid detection of pitting, crevice corrosion, cracks, and flaws.

The disadvantages of AE technique are: complicated devices, skilful and knowledgeable personnel, and expertise are needed; environments are generally noisy, and the AE signals are usually weak, thus, signal discrimination and noise reduction are difficult, yet extremely important for successful AE applications. In spite of developing quantitative AE technique, in most cases, commercial AE systems can only estimate qualitatively how much damage is in the material and approximately how long the structures will serve. Thus, other NDT methods are needed to do more thorough examinations and provide quantitative results.

8.1.3 Magnetic and Electromagnetic Methods

Magnetism is the ability of a matter to attract other matter to itself. The ancient Greeks probably were the first to discover this phenomenon in a mineral they named magnetite. Later other ferromagnetic materials (iron, nickel, cobalt, and some of their alloys) were discovered. They are materials that can be magnetized to a noticeable extent and can allow the inspection to be effective. Cannon barrels

were checked in 1868 for defects by magnetizing the barrel then sliding a magnetic compass along the barrel's length. These early inspectors were able to locate flaws in the barrels by monitoring the needle of the compass. It was discovered in the early 1920's that a surface or subsurface flaw in a magnetized material caused the magnetic field to distort (to 'leak') and extend beyond the part. This is the principle of magnetic flux leakage and magnetic particle inspection.

Magnetic flux leakage (MFL) is a magnetic method of NDT that is used to detect corrosion in steel structures, most commonly in tank bottoms and pipelines determining from which side corrosion occurs. The basic principle is that a powerful magnet is used to magnetize the steel. Corrosion defects (pits, cracks) result in a distortion of the magnetic field ('leakage') at the steel surface. This distortion is detected by MFL detectors. In an MFL tool, a magnetic detector is placed between the poles of the magnet to detect the leakage field. Analysts interpret the chart recording of the leakage field to identify damaged areas and hopefully to estimate the depth of metal loss. MFL inspection pigs are equipped with a circumferential array of strong permanent magnets to magnetise the pipeline wall (see Sect. 8.4). The magnets are coupled to the internal pipe wall by means of brushes. Both internal and external corrosion (depth and geometry) can be detected with MFL technology.

Magnetic particle inspection (MPI) uses magnetic fields and small magnetic particles (i.e., iron filings) to detect flaws in ferromagnetic materials. The magnetic lines of force are running from the south to the north pole in a magnetized material. These lines are interrupted and leave the metal at locations of defects. At these locations compounds which can be magnetized, like iron particles (generally with fluorescent agent), are attracted. The iron particles concentrate at locations of leaving lines of forces and indicate defects (for instance, cracks). MPI is really a combination of MFL and visual examination.

Magnetic induction is based on magnetic induction principle of ferromagnetic materials and is used for measurements of non-magnetic layers on ferromagnetic materials (e.g., aluminum, stainless steel, or organic coating thickness on carbon steel). These devices are called dualscope or permascopes. Electromagnetic methods (sensors) are used as computerized NDT for CM in tanks, pipelines, and under organic coatings [22–24]. Electromagnetic acoustic transducers based on physical effects Lorentz force and magnetostriction are developed as an in-line inspection tool for the detection of SCC and coating disbondment [25].

8.1.4 Eddy Current Technique

Eddy currents (EC) are electric currents induced within conductors by a changing magnetic field in the conductor. They are also called Foucault currents in memory of French physicist Léon Foucault (1819–1868) who discovered them in 1855. The term *eddy current* comes from analogous currents (vortices) that we see in water when dragging an oar. Circulating eddies of electric current have inductance and thus induce magnetic field. EC technique uses an electromagnetic field generated by an electrical coil mounted in a probe. The alternated electromagnetic field in-

duces EC in a conducting material (e.g., tube wall). The induced EC in return generate an alternating electromagnetic field opposing the original electromagnetic field, and results in a change in coil impedance, which is measured by the EC instrument. The change in coil impedance depends on the amount of metal loss or the depth of defects (pits, cracks). By calibrating the EC instrument the defects are measured with high accuracy. EC technique is a non-contact one using for measuring general corrosion, e.g., detection corrosion under thermal insulation [26].

Some physical methods cannot be used under insulation at high temperatures ($> 100^{\circ}\text{C}$). In such cases *ultrasonic guided wave*, *pulsed eddy current*, *radiography*, and *infrared thermography methods* are used.

Pulsed Eddy Current (PEC) employs a pulsed magnetic field to generate EC in the steel. Since carbon steel is ferromagnetic, only the top layer of the steel is magnetized. The eddy currents diffuse into the test specimen until they eventually reach the far surface. Then they induce a voltage signal in the receiver coils of the PEC probe. As long as the EC experience free expansion in the steel, their strength decreases relatively slowly. Upon reaching the far surface, their strength decreases rapidly. The moment in time when the EC first reach the far surface is indicated by a sharp decrease in the PEC signal. The onset of the sharp decrease point is a measure of wall thickness. An earlier onset of this sharp decay of one PEC signal compared to a reference signal indicates wall loss. PEC is a non-intrusive and non-contact NDT method, therefore can be applied for wall thickness monitoring at temperatures up to 540°C [27]. PEC has a much better reproducibility than ultrasonic wall thickness measurements and has been applied to monitor wall thickness in piping of refineries and oil production platforms.

8.1.5 Other Physical NDT Methods

Acoustic Pulse Reflectometry is the technique when a wideband acoustic pulse is shot into the tube and any reflections that are created by changes in the cross section of the tube are recorded by a microphone. This method allows detecting any fault in tube systems: pits, holes, wall thinning, and deposits [28].

Acoustic, vibro-modulation technique, based on non-linear interaction of ultrasound and vibrations in the presence of defects, is developed for non-destructive detection of SCC, corrosion-induced delamination of structural elements, fatigue cracks in various materials (metals, polymers, composites), debonding, and crevice corrosion [29]. One of the unique features of this technique is its ability to differentiate cracks, delaminations and debonding from notches, voids and other heterogeneities because of specific non-linear interaction which occurs only at the contact-type interface.

Non-linear elastic wave spectroscopy is developing for detection SCC [30]. In the presence of stress corrosion damage the material starts to behave non-linearly around the damage location. This behavior manifests itself up in the bi-harmonic

excited signal spectrum as sidebands and harmonics of the excited frequencies. The magnitude and number of these effects are related to size of damage.

NDT allows monitoring uniform and localized corrosion. Advanced NDT, *multi-array Automated Ultrasonic Testing* and *Swept Low Frequency Eddy Current*, are used in oil refineries for detailed mapping of the inspected surfaces that resolve small pits [31].

Penetrant testing is based on the properties of some liquids containing a contrasting (generally red colored) or fluorescent compound to penetrate in small defects. After removing the redundant penetrant liquid a developer is applied. The developer is a white powder with absorbing properties. The remaining penetrant in the defect is sucked into the developer and indicates the failure (cracks) in metals, ceramics, and polymers.

X-ray radiographic methods (radiography) use X-rays (are emitted by outside electrons) or gamma-rays (are emitted by the nucleus) and can detect general and localized corrosion. *Flash radiography*, using short pulses of X-rays, allows detecting corrosion under insulation. X-ray radiographic methods are used for on-line wall thickness measurements of insulated pipes and tanks [32, 33]. Radiography has the disadvantages that it can be a safety hazard and is poor at detecting cracks.

Infrared thermography. All objects emit infra-red (IR) radiation and the amount of radiation increases with temperature. The IR radiation is a part of the electromagnetic spectrum, not visible to the naked eye, but can be viewed with IR camera. When viewed by a thermographic camera, warm objects stand out well against cooler backgrounds. As a result, thermography makes it possible to “see” an object, without visible illumination. *Thermography* is a type of IR imaging. IR cameras detect radiation in the IR electromagnetic spectrum and produce images of the surface with information about the surface temperatures or temperature differences. IR is used as a visual technique for the identification real or potential corrosion. IR technology is used for detection temperature deviations, namely, hot or cold spots at pipes and other equipment, diagnosing corrosion in refinery’s units, and monitor blisters under organic coatings [34–36]. The IR technique has limitations: surface conditions (dirt, reflection, rust and other deposits formed on the surface) influence results; weather conditions (e.g., strong wind) can completely obscure thermal data.

On-site chemical analysis of alloys. Often we need to know the type of a metal/alloy, concentration of alloying elements and even concentration of carbon, sulphur, phosphorous, silicon, and some other elements in alloys of tanks, pipes, or other construction and equipment. Handheld (portable) devices based on *X-ray fluorescence (XRF) spectroscopy* and *optical emission spectrometry* for fast *on-site non-destructive chemical analysis* of alloys are used. *XRF spectroscopy* is the emission of characteristic ‘secondary’ (or fluorescent) X-rays from a material that has been excited by bombarding with high-energy X-rays or gamma rays. This technology analyzes the composition of alloys by measuring the spectrum of the fluorescent X-rays. Each of the elements present in a sample produces a unique set of characteristic X-rays that is a “fingerprint” for that specific element. XRF analyzers allow measuring low concentrations (ppm!) of elements in alloys of metallic constructions. All that is necessary for analysis is to expose the surface of structure or

equipment to the instrument for a few seconds, and then read the final identification from the display [37].

Optical Emission Spectrometry (OES), also called *Atomic Emission Spectroscopy (AES)* or *arc spark emission spectroscopy*, is based on the emission spectrum of a chemical element which is the spectrum of frequencies of electromagnetic radiation emitted by the element's atoms when they are returned to a lower energy state [38]. Portable *OES* alloy analyzers are used for fast elemental analysis of metals and alloys providing carbon content and identification of steel grades.

Radiography, *pulsed eddy current*, *longrange ultrasonics*, and *thermography* are used in detecting of corrosion under insulation [39–41]. Mathematical model is developed for prediction of the number of susceptible locations which will need to be refurbished [42].

8.1.6 Weight Loss and Electrical Resistance (ER) Methods

Weight Loss (WL) method is based on the insertion of metallic specimen called *coupons* of known mass and area in a process stream, immersion during some period (usually 30–300 days), removing, cleaning from corrosion products and other deposits and weighing. The difference in mass of the coupon of known area and immersion period is the corrosion rate of this metal in the media. The WL method is standardized [43–47], widely used for corrosion rate determination in aqueous and two phase hydrocarbon-water media [48–51] and for determination of corrosivity of soils [52, 53].

Electrical Resistance (ER) method is based on the measurements of electrical resistance of metal specimen (sensor) which increases when corrosion occurs (cross-sectional area A decreases):

$$R = \rho \times L / A \quad (8.1)$$

R —the electrical resistance of metal specimen, Ohm; ρ —the specific electrical resistivity of metal specimen, Ohm·m; L —the length of a specimen, m; A —the cross-sectional area of a specimen, m².

Really this method is analog of the WL method. Sensors in the ER-probes are made in a variety of geometric configurations (wire, strip, tube, cylindrical, and flush), thickness and alloy materials, and they are called *corrosometers*. Flush probes are suited for pipelines, where pigging may occur, and for bottom off-line monitoring in oil and gas, or multiphase flows where the corrosive water phase exists [54]. The choice of ER-probes depends on aggressiveness of the environment. The ER method is standardized [55], widely used for corrosion rate determination in the overhead of crude distillation units in the oil refining industry [48–51], in hydrocarbons [56], for monitoring the efficiency of cathodic protection of fuel storage tank bottoms [57] and underground pipelines [58, 59], and for internal CM of subsea production flowlines [60]. The design of ER-probes permits operation up to 537°C and 700 atm. [61].

WL and ER methods can be used for CM in systems containing fuels. However, if there are no water, dissolved oxygen and other corrosive components in fuels corrosion rates are very low and long time is needed to get some reasonable results and information about corrosion rates. WL method and ER probes are not applied for CM in tanks containing fuels. However, ER probes using for CM in the atmosphere can be used also in gaseous phase in tanks.

Most physical methods have limitation: they assume that corrosion rate is constant throughout the entire exposure period. In reality, damage rarely happens at a continuous rate but rather takes place in discrete episodes that can be correlated with specific operational events [62]. Many physical techniques are labor intensive and expensive. For instance, it was estimated that 35 % of a plants maintenance budget is spent on the cost of UT inspection or on physically opening tanks and other vessels for visual inspection [63].

8.2 Examination and Control of the Environment

Examination and control of the environment include chemical analytical, physico-chemical, physical, and microbiological analysis of media (crude oil, fuels, water, two-phase solution, gaseous phase or soil) which contact surface of tanks and pipes. These methods are used for the determination of aggressive components and their amounts in media: pH, Cl^- , SO_4^{2-} , O_2 , CO_2 , H_2S , NH_3 , suspended solids, microorganisms influencing corrosion; the presence of contaminants inducing erosion in pipes. For fuels, it is important to measure water content, dissolved oxygen concentration, sulphur-containing compounds, and electrical conductance; total acid number, total sulphur and nitrogen, the concentration of salt and water, and sometimes microorganisms in crude oil; chemical and microbial composition of deposits (biofouling) at the bottom of the tanks and in pipes. Oil refineries combine WL and ER methods with chemical analytical methods of streams.

The question is what are the dangerous values of analytical parameters (pH, iron, copper, chlorides, microorganisms, etc.) determining corrosion intensity (high or low) in the system?

The permissible values depend on specific system (type of materials and media used) as well on corrosion type. In many cases, it is important to monitor not absolute values, but their trend. That is sudden changes of these values can show beginning of corrosion.

The analysis of residue concentrations of corrosion inhibitors, neutralizers, oxygen and hydrogen sulphide scavengers, fuel additives, biocides in fuels and drain water is important for control of the efficiency of anti-corrosion treatment, as well for ecology.

Control of process (technological) parameters includes the measuring of flow rate, temperature, pressure, and dewpoint temperature.

The benefit of chemical analytical methods is high sensitivity to all metals dissolved in liquids. The disadvantages are: chemical content of corrosive

components in the environment gives qualitative estimation of corrosion situation; the presence of corrosion products on metallic surface can give rise wrong results; these methods require sometimes much time for obtaining results.

8.3 Control the Interphase Metal–Environment

These methods are based on the physico-chemical properties of the interphase metal–environment, and may be divided into electrochemical methods, identification of corrosion products and deposits, and examination of the morphology of the metal surface. Electrochemical methods (measuring of electric potential and currents) cannot be used in fuels as they are not electrolytes (except fuel alcohols). However, measuring of electric potential of underground and submerged structures with applied cathodic protection is the main criteria in monitoring the efficiency and integrity of the cathodic protection (see Sect. 8.5).

Scanning Electron Microscopy (SEM), Scanning Tunneling Microscopy (STM), and Atomic Force Microscopy (AFM) are used for the examination of metal surface morphology. Energy Dispersive Spectroscopy (EDS), Energy Dispersive X-ray Fluorescence (ED-XRF), X-ray Photoelectron Spectroscopy (XPS), also known as Electron Spectroscopy for Chemical Analysis (ESCA), Auger Electron Spectroscopy (AES), Mössbauer Spectroscopy, Secondary Ion Mass Spectroscopy (SIMS), Fourier Transform Infrared Spectroscopy (FTIR), Raman spectroscopy, UV-Visible reflectance studies, and Ultraviolet Photoelectron Spectroscopy (UPS) are used for the identification of corrosion products, deposits and corrosion inhibitors on metal surface. Microbiological analysis of deposits (sessile bacteria on metal surface) also is important. These analyses can give information about the causes of corrosion and thus the ways of its prevention.

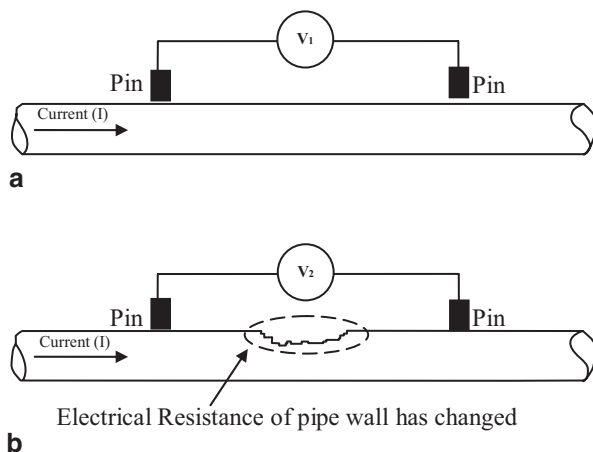
8.4 On-Line, Real-Time CM

Corrosion rate is a number inversely proportional to the corrosion engineer's remaining tenure on the job. (Joke of corrosionists)

On-line measurements are continuous control of metal loss, corrosion rate, and physico-chemical parameters in a system; data are obtained without disrupting of monitoring process. *Off-line* measurements are periodical control in a system with disrupting of monitoring process. *Real-time* information is corrosion rate data that can be obtained instantaneously, or with more frequency than the changes in the parameter being investigated; these data are usually obtained during several minutes.

CM allows rapid determination of changes in physico-chemical parameters of process stream including environmental factors (temperature, pressure, flow rate, chemical feed rate).

Fig. 8.2 Scheme of the FSM technique: **a** no corrosion; **b** corrosion occurs



On-line, real-time CM must be integrated with the process control system, i.e., technological parameters should be monitored together with corrosion data [64–66]. The pertinent operating and analytical data are entered into the risk matrix analysis where the data are used to develop the relative risk and the consequence of the corrosion [67]. CM technology can determine uniform and localized corrosion, even when the uniform corrosion rate is low. On-line, real-time CM is used for pipelines and rarely for tanks and other equipment contacting fuels. Some of these CM systems are described below.

The *Resistance Corrosion Monitoring* (RCM) device is used for continuous monitoring of pipe wall thickness [68–70]. The RCM operates on the same principal as traditional ER probes except it utilizes the pipe wall as the active sensor element, and it provides much more accurate data. The RCM is an array of pins welded directly onto the pipe, covering approximately 1 m² area of pipe to be monitored.

The *Field Signature Method* (FSM) is based on feeding an electric direct current through the selected sections of the structure to be monitored and sensing the pattern of the electrical field by measuring small potential differences set up on the surface of the monitored object [71]. The current feed points are located 1–3 m apart. Sensing pins are used to measure the voltage response to an induced current (Fig. 8.2).

This type of measurement between two pins is closely related to an ER measurement. For a metal with an even wall thickness, without flaws or defects, a uniform electrical field is set up, reflecting the wall thickness. The uniform corrosion, pits, and cracks distort this electrical field, reflecting the reduction in the pipe wall thickness. Proper interpretation of electric potential differences can lead to conclusion about wall thickness reduction. The FSM provides on-line information on wall thickness loss, erosion, cracking, or pitting, and is used on subsea pipelines, storage tanks, and refineries units up to 450 °C [72–74].

Advanced ER on-line corrosion probes with fiber optic communication links is used for the measuring of the effectiveness of the chemical treatment program in

gas, oil, and water flooding plants [64]. This system is connected to 10 stand-alone servers linked to more than 300 transmitters/probes. The distance between the furthest monitoring site and the server is ~ 150 km. Remote seats are also provided with the software to allow users to access the corrosion server remotely. This system is ~ 256 times more sensitive to corrosion rate changes and less sensitive to temperature fluctuations than traditional ER systems.

Both external and internal surveys are used for evaluating the condition of pipelines. The *in-line inspection* (ILI) tools are a common method to evaluate pipelines and pinpoint damage [75]. The ILI surveys provide information on wall thickness changes caused by corrosion, welds, branch connections, and valves in the pipe. The internal corrosion in pipelines is assessed by following NDT [76–86]:

- a. “Intelligent (smart) pigs” and verification by excavation and detailed examination at selected sites. “Pigs” (scrapers) are devices that are inserted into the pipeline and perform dedicated functions as they travel through the pipeline. They can detect different corrosion damages, cracks, and leaks in pipelines [87–91].
- b. Magnetic and electromagnetic techniques (including MFL), UT (including guided wave UT), and eddy currents [86, 88, 92–98]. The “pigs” can use either permanent magnets or electromagnets.
- c. The in-line inspection in unpiggable pipelines, based on the fluid flow modeling and the determination of the critical pipeline inclination angles that may be likely sites for water accumulation [99, 100], and by means of high-resolution defectoscopes [101, 102].
- d. The field signature method (FSM) [103–105].
- e. Carbon-silver galvanic couple thin-film sensors for the indication of water accumulation possessing corrosion risk in pipelines [81].
- f. The fiber optic sensors for monitoring uniform and pitting corrosion in real-time [106, 107].
- g. The finger probes with pressure gauges, the ER probes, and acoustic devices for the detection of erosion inside of pipelines [108–110].

The main limitation of most of these techniques is the need to have a prior knowledge of the optimum location for sensors. Integrity management and current technologies include all data that support the estimation of corrosion situation in the pipelines, namely, direct data (corrosion rate) and indirect data (chemical composition of media, presence of microorganisms, operating conditions, flow rate, flow regime, etc.) [111–115]. Software models can predict corrosion rate for any point along a pipeline.

Contactless immersion ultrasound modules (UT method) based on the clamp concept are used for real-time corrosion of pipelines [92]. If one distributes a number of transducers around the pipeline it will be possible to detect localized corrosion [93]. The ER probes are used for CM of external corrosion of underground pipelines [59, 116].

The corrosion sensor utilizing the *resistive strain gauge* or an *optic fiber* instrument for the measuring of the *diaphragm deflection* as an indication of sustained corrosion damage inside of pipelines is developed [117–119]. The sensing element

(test diaphragm) is constructed of a material similar to the monitored pipe wall. As the test diaphragm thins due to corrosion, it becomes more sensitive to pipeline pressure and deflects accordingly.

The “intelligent” system including *fiber optic sensors* is developed to monitor internal corrosion, cracking and crack propagation, temperature and pressure changes, pH and dissolved CO₂ concentration, as well to detect leaks, buckling, bending and soil movement (environmental condition changes of a pipe) [82, 119, 120]. Thus, combination of physical, chemical and physico-chemical methods is optimal and useful for CM of pipelines.

8.5 Monitoring of Cathodic Protection

Monitoring and the examination of efficiency of cathodic protection (CP) of external surfaces of AST in contact with soil or sand and UST are defined by standards [121–126]; underground and submerged metallic piping systems and evaluation of underground pipeline coating condition are defined by standards [127–129]. Two criteria for corrosion control of carbon steel structures under CP exist. The first criterion is a negative (cathodic) potential of at least 850 mV measured with respect to a saturated copper-copper sulfate reference electrode contacting the electrolyte. The second criterion is a minimum of 100 mV of cathodic polarization between the carbon steel surface of the protected structure and a stable reference electrode contacting the electrolyte. In electrical potential measurements, reference electrode must be installed on the ground and not on concrete or asphalt. Sometimes stationary reference electrodes are installed for measuring potentials under the tank. Coupons and ER probes also can be used in evaluating the effectiveness of the CP system.

Close Interval Potential Survey (CIPS) and Direct Current Voltage Gradient (DCVG) techniques are widely used for monitoring of efficiency of CP of buried pipelines [130–134]. CIPS is carried out to provide a profile of the potential level throughout the length of pipelines and other buried or submerged metallic structures. DCVG is based on measuring the voltage (potential) gradients in the soil above a cathodically protected pipeline. When impressed current is applied to a pipeline under CP, a voltage gradient is established in the ground due to the passage of current through the soil to the bare steel exposed at a coating fault. The voltage gradient is measured between two similar reference electrodes (usually copper-copper sulphate) at the distance of ~1 m. The greater the size of the defect, the greater the voltage gradient. Coating faults as small as a fingernail can be located to within a few centimetres on pipelines buried 1–2 m deep. DCVG helps determining deficiency in CP and coating faults (holidays).

Visual inspection inside of shipboard tanks demands drainage, opening, and venting. In order to monitor efficiency of CP and protective properties of coatings inside of shipboard tanks without all these labor and time-consuming procedure the measuring of corrosion potentials of metallic tank surface and electrical currents between anodes and tank surface are used.

Table 8.1 Maximum recommended intervals between inspections of tanks

Service conditions	Externals	Internals	
	Ultrasonic thickness, years	Sample or single tank, years	Maximum for group, years
Slops, water, brine, corrosive or aggressive chemicals. No coating	1	3	10
Slops, water, brine, corrosive or aggressive chemicals with proven internal coating	5	7	12
Crude oil, intermediate light petroleum products (naphtha, gasoline); treated water	5	8	16
Gas oil, fuel oil, lubricants, grease; inert or non-aggressive chemicals	8	16	20
Jet fuel (fully coated)	10	15	30
Gasoline, kerosene (jet fuel) (uncoated)	5	10	20

Regular visual external inspection of AST must be carried out once a month

8.6 Inspection of Tanks

The test methods, monitoring, inspection checklist, inspection frequency, and corrosion control of new AST during their design and construction, and of existing AST during inspection, maintenance and repairs are described in standards [135–137]. In-service inspection includes a visual inspection of external and internal surfaces of AST and measuring of thicknesses of shells and roofs inside and outside AST by different physical methods (see Sect. 8.1). Recommended intervals between inspections of tanks are shown in Table 8.1.

A visual inspection of the outer surface includes the presence of leakage, the appearance of corrosion (rust and pits), the state of the coating and insulation, and signs of deterioration of the tank foundation. Corrosion rates based on measurements of thickness should be calculated. The measurements of thicknesses usually are carried out using UT. It is recommended to carry out inspection (visually and by means of video camera) of inner coatings after 10 years after its implementation (performance) and then every 5 years. Inspection of the internal surface of AST containing fuels is recommended every 16–20 years (see Table 8.1). Before inspection, tank bottom must be cleaned from any sludge and inner space must be ventilated. Examination and inspection of AST is important for detection of corrosion damages and decision about further prevention and exploitation. The examination of the state (situation) of existent coatings in AST is described in standard [138]. The selection of coating systems is carried out according to corrosion situation of the bottom, shell, and roof (see Sect. 7.2 and Appendix L).

8.6.1 Conclusion

The NDT and CM must be an important part of pursuing, detecting, prediction and prevention corrosion of systems containing fuels. We should differentiate CM from inspection and survey. In spite of the latter is planned and organized periodically, CM is carrying out on-line, and we can obtain information about corrosion situation in real-time. The NDT and CM are the multi-disciplinary issue, covering a wide range of measurement techniques, sensors, devices, instrumentation, data analysis, and standards. The general philosophy of NDT and CM is that multiple techniques are used to both complement and check each other. Many CM techniques are available, but relatively few are in a widespread use. The choice of CM method depends on type of equipment and structure, conditions, and objectives. Therefore, there is no one absolute recommendation for all systems. You should try to use as more CM methods as you can. Use of the NDT and CM can effectively reduce the failure risk to nearly zero. In some cases, visual inspection will not observe anything until a significant damage has developed, which causes a high cost of repair in the short term. Therefore on-line real-time CM is needed. There is no single technology that can detect and monitor all types of corrosion damage, as many corrosion types exist (uniform or specific localized types). Universal NDT and CM system (device) for all corrosion phenomena and cases hardly will be created.

The NDT and CM must be planned and carried out at the stage of design and project. It is very important correctly select NDT and CM type and inspection points. NDT, for instance ultrasonic thickness measurements, must be taken in the vicinity of the CM points. Corrosion rate even for uniform corrosion may be significantly changed at different distances. The more places we monitor, the more complete and the more real corrosion situation may be determined. It is out of place to say about high cost of CM techniques. CM occupies only $\sim 0.05\%$ of cost from corrosion in oil refining industry. When corrosion occurs, cost of damage usually is thousands times more than application of CM. NDT and CM data (thicknesses and corrosion rates) enter and appear on monitors as other technological parameters: temperature, pressure, flow rate, and concentration of chemicals. Corrosion thermodynamics is understood well and theoretically corrosion may be predicted, but corrosion kinetics is based only on experimental data. Just in few cases corrosion rate and remaining lifetime can be predicted based on the NDT and CM data. The key factor of successful NDT and CM is the determination of the “areas of interest” (dangerous places or points), and this demands close cooperation of plant inspection departments, corrosion engineers, plant operators and processing engineers. We should remember that any corrosion sensor measures corrosion only in a local place and we do not know exactly what happens in the vicinity. That defines some vagueness in general philosophy of NDT and CM.

There is resemblance between corrosion rates and the results of stock exchanges; results from the past are not guarantee for the future. Any changes in processing (temperature, installation additional pumps, changes of diameter of pipelines and tanks, fuel or crude oil type, inhibitors, neutralizers and other chemicals) can result

in sudden increase of corrosion. Therefore, we should analyze any changes, how they can influence corrosion situation. In this light, CM and NDT play important role in keeping metallic constructions in good conditions and preservation people and environment from catastrophes.

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Chapter 9

Cases of Typical and Unusual Corrosion of Tanks

One example equals to thousand generalizations.

The Folk wisdom.

Abstract Ten cases of corrosion failures of tanks containing different petroleum products with relevant pictures, analysis of the causes and solutions are given.

9.1 Corrosion of Outer Surface of Tanks’ Shell Under Bricks

Three cases of corrosion of tanks’ surface under bricks are described below.

9.1.1 Case 1

Small AST (2,000 m³) usually are intended for storage petroleum products or slops. Slops are the mixture of petroleum off spec products from kerosene to fuel oil, water and slurry which must be reprocessed. These AST shells were made of six carbon steel strips surrounded by the bricks and were in service 70 years (Fig. 9.1).

The diameter and the height of the AST were 12 m. The original thicknesses of the first three strips were 6.36 mm and the other three courses were 4.76 mm. The tanks were erected on the concrete basement. In rare cases, AST are surrounded by bricks. For instance, all AST in one refinery were surrounded by the bricks against bomb attack in 1940. The wall of brick blocks also served well against heating by sunlight in south regions and resulted in diminishing of evaporation of petroleum products/slops during their storage in carbon steel tanks. As well oxidation of hydrocarbons also decreased. Bricks were erected around the AST nearly to its top (roof) (see Fig. 9.1a). When wetness with the fuel smell was detected on the outer surface of bricks they were removed (Figs. 9.1b, c) and severe corrosion was revealed up to large holes on the outer surface of the shell at the height of 1 m (Fig. 9.1d). Measur-



Fig. 9.1 AST (2,000 m³) for storage petroleum products/slops with surrounded bricks. **a** Upper part of the AST. **b, c, d** Failed AST location—corrosion under bricks at 1 m height of the shell at the south side of the AST

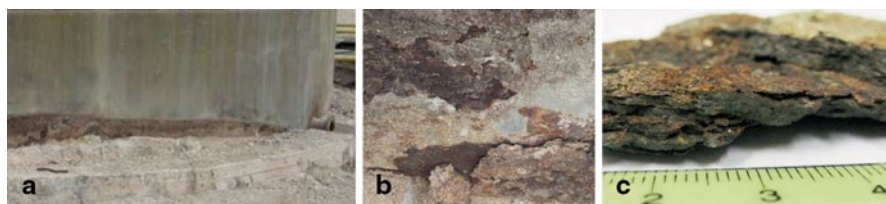


Fig. 9.2 **a** Corroded bottom and the 1st strip of the AST on the concrete basement. **b** Magnification of Fig. 9.2a. **c** Thick rust on the outer surface of the first strip of the shell

ing of shell thickness showed its drastic diminishing from 6.36 mm to nearly zero (after 70 years of service).

9.1.2 Case 2

After removing the bricks around the shell of similar small AST, severe corrosion and rust of 11 mm of thickness were detected outside the bottom of the tank from the basement to the height of 0.5 m after 70 years of service (Fig. 9.2).

9.1.3 Case 3

After removing the bricks around the shell of large AST (13,450 m³) containing fuel oil, severe corrosion and rust of 10 mm thickness were detected outside the bottom of the tank from the basement to the height of 0.3 m after 63 years of service (Fig. 9.3).

The lower side of the large AST was in contact with soil. The wall thickness decreased from 18.2 mm (original) to 7 mm whereas minimum allowable thickness calculated according to API 653 is 13.2 mm (see Appendix J).

Cause of failures in three cases The cause of corrosion in three cases above is penetration of rain and condensed water between carbon steel shell and bricks/soil. Rain water entered between bricks and outer surface of the upper part of the shell and



Fig. 9.3 **a** Outer surface (*lower* part) of the shell of the large AST of contact with bricks and soil. **b** Magnification of **a**: loose thick rust (10–12 mm thickness) is marked. **c** Magnification of **b**

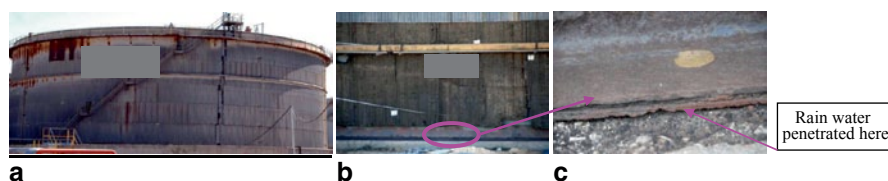


Fig. 9.4 **a** Corroded galvanized sheets after 26 years of service in the atmosphere of the oil refinery. **b**, **c** Corroded outer surface bottom of the AST shell contacting concrete basement (the chime area)

retained inside (see Fig. 9.1a). Corrosion of outer surface of the shell under bricks occurred according to electrochemical mechanism with the participation of water and oxygen. If to take into consideration that the design life of AST surrounded by bricks is 25–30 years, such long service life of 63–70 years of the AST around the wall is reasonable.

Solution Isolation of the top part of the tank where wall of bricks is in contact with the roof and shell by flexible visco-elastic protective waterproofing coating. Outer surface of shell under bricks should be painted.

9.1.4 Case 4. Outside and Inside Corrosion of the AST Containing Gas Oil

The carbon steel AST was in service 26 years at the oil refinery. Its dimensions: the diameter—36.6 m, the height—12.8 m and the volume—13,450 m³. It contained gas oil at ambient temperature during the first 23 years and heavy vacuum gas oil (heavier petroleum products than conventional gas oil) at ~90°C during the last 3 years of service. Outer surface of the shell under glass wool thermal insulation was painted and covered with galvanized sheets (Fig. 9.4). Severe outside (galvanized sheets and the chime area of the tank) and inside corrosion on the bottom was detected after 26 years of service.

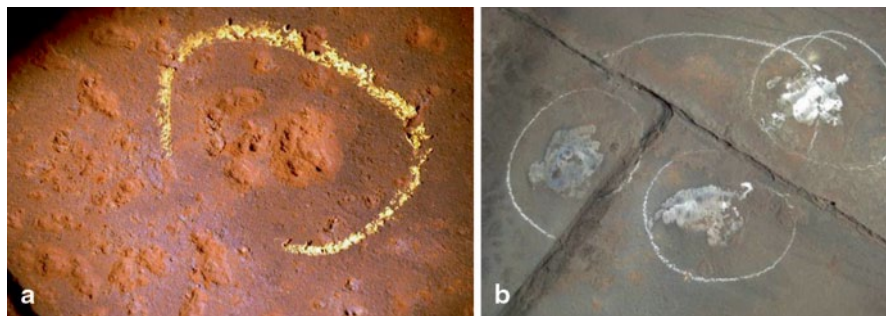


Fig. 9.5 **a** Pitting corrosion (as a result of MIC) of *inner* surface at the bottom of the gas oil AST. **b** Corrosion of welds on the bottom of the gas oil AST

Outside corrosion of galvanized sheets Galvanized sheets were corroded as a result of atmospheric corrosion (Fig. 9.4a). The atmosphere at the oil refinery usually contains certain amounts of H_2S which attacks galvanized steel (zinc is not resistant to H_2S).

Outside corrosion of the chime area The bottom of the AST which contacted concrete basement ring (the chime area) was severely corroded (Fig. 9.4b, c). Usually AST are built on a concrete ring and the bottom plates are resting on it. Movements of metallic parts of AST during filling and emptying of the fuel usually occur and therefore a gap between the concrete ring and the bottom plate is very common. If the chime area is not sealed, water can penetrate between the bottom plate and the concrete ring bed, creating a corrosive environment.

Cause of failure Rain water entered into the space between the annular plate (bottom of the AST) and the concrete basement ring (underneath the bottom plate), retained for a long time and resulted in corrosion that occurred according to electrochemical mechanism with the participation of water and oxygen.

Solutions Not galvanized, but aluminized sheets (hot-dip aluminized steel) or aluminum foil wrapping should be used under atmosphere with H_2S contamination (aluminum is resistant to H_2S). Coating under thermal insulation must be applied (see Appendix L, Table L.4).

Flexible visco-elastic protective waterproofing coating at the chime area of tanks should be used for prevention of water ingress between steel annular plate and concrete basement ring (sealing the gaps on AST bottom). This chime sealant system remains flexible and tacky, and allows movements due to flexing of bottom plates which move during the filling and emptying of fuels in tanks.

Inside corrosion Thick sludge was found on the bottom of the gas oil AST which contained large amounts of heterotrophic bacteria. Inner surface of the bottom and weld zones in the gas oil AST were severely corroded (Fig. 9.5a, b).

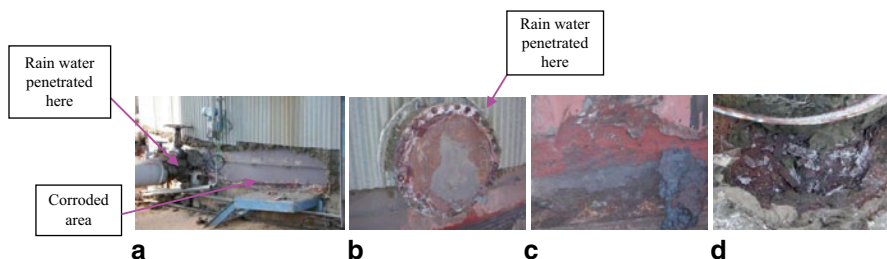


Fig. 9.6 **a** Lower part of the asphalt AST. **b** Rusty manhole. **c** Magnification of Fig. 9.6b. **d** Rust with glass wool

Cause of failure MIC was the cause of localized corrosion at the bottom. Usually welds are the first attacking by MIC because of their metallurgical and electrochemical heterogeneity.

Solution Periodical cleaning of inner surface bottom of gas oil AST from sludge and coating performance (see Appendix L).

9.1.5 Case 5. Corrosion Under Thermal Insulation of the AST Containing Asphalt

Leak was detected from the bottom of the carbon steel AST containing asphalt which was 23 years in service. Outer surface of the tank was painted and thermally insulated by glass wool. The tank was erected on the concrete ring. Asphalt inside the tank was heated to 100 °C for prevention its solidification. Severe corrosion with thick rust (~10 mm) was detected on the outer surface of lower part of the tank and the manhole (Fig. 9.6). Coating disappeared under the thermal insulation.

Cause of failure The phenomenon *corrosion under thermal insulation* occurred (see Sect. 5.9). The rain water and oxygen entered through non-hermetic covers installed on the valve and the manhole, were “captured” under the thermal insulation and could not egress in opposite direction. As a result electrochemical corrosion with the participation of water and oxygen occurred at ~90 °C.

Solution Appropriate coating under thermal insulation (see Appendix L, Table L.4). Thermal insulation must have good jacketing, providing mechanical and weather protection of the insulation. Application of mastics, sealants and caulks. Sealing of the chime area between shell and concrete ring basement. Regular inspection and correct maintenance.

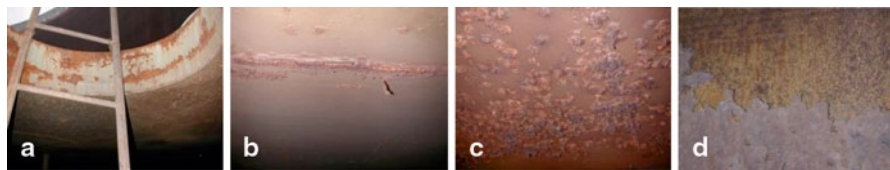


Fig. 9.7 Inner surface of the floating roof in gasoline AST after 12 years of service: **a** Inlet in the floating roof (failed epoxy coating and rust). **b** Rusted weld blisters and rust. **c** Failed epoxy coating and rust inside the floating roof. **d** Rust and failed epoxy coat on the inner surface of the shell (1 m height)

9.1.6 Case 6. General Corrosion and Coating Failure in Gasoline AST

The gasoline AST equipped with floating roof and pontoon was in service 12 years. Inner surfaces of the bottom and the shell (to the height of 1 m), inner and outer surfaces of floating roof were coated by epoxy paint with thickness of 200 μm . Inner surface of the shell at the height above 1 m which was not painted was severely rusted. The coating failed, blisters and rust were detected under the coating, especially in the welds and on the shell at the height of 1 m (Fig. 9.7). The *cause of coating failure* was insufficient thickness of 200 μm epoxy coating.

In spite of failure of epoxy coating and rust formation, thicknesses of carbon steel shell, bottom, pontoon and floating roof were not changed significantly. Epoxy coating protected inner surfaces of gasoline AST during 12 years of service.

Solution Recoating with epoxy coating with thickness 550 μm (see Appendix L, Tables L.1 and L.2).

9.1.7 Case 7. General Corrosion and Coating Failure in the AST (separator)

The carbon steel AST was served for separation of water and crude oil remains during 9 years. Inner surface of the bottom was coated with epoxy paint with thickness 300 μm . Steam was used for the cleaning of AST inner surface therefore temperature sometimes increased to 90 °C. Severe general and localized corrosion, especially in the weld zones of inner surfaces of the AST (separator) was detected (Fig. 9.8). Rust and black iron sulphides are formed on the inner surface of the shell. Blisters in the coating and shallow pits underneath were detected on the bottom.

Cause of corrosion and coating failure use of steam (90 °C).

Solution Painting with epoxy phenolic or epoxy novolac coating system with thickness 550 μm (see Appendix L). These coating systems are resistant to crude oil-water mixture to 100 °C.

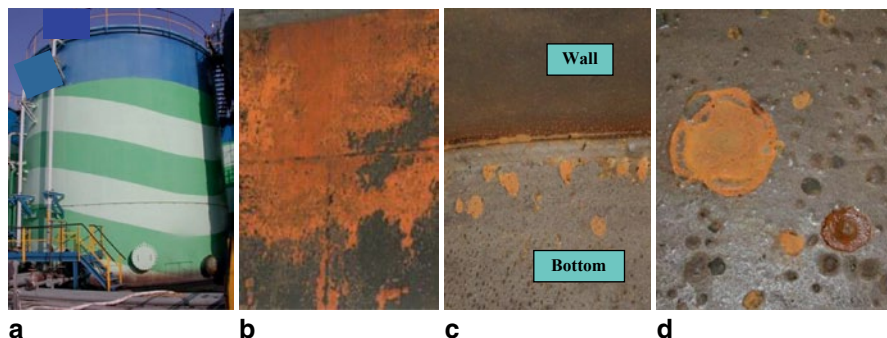


Fig. 9.8 **a** General view of the AST (separator), **b** Corroded inner surface of the shell, **c** Corrosion and failed coating on the wall and bottom, **d** Failed coating on the bottom



Fig. 9.9 Inner surface of kerosene AST after 6 years of service: **a** The bottom before cleaning (grey-black slime and rust); **b** The bottom after cleaning (blue mill scale; black corrosion hole is marked by the circle); **c** Shell

9.1.8 Case 8. Inner Corrosion of AST Containing Kerosene

The carbon steel AST containing kerosene has been in service for 6 years. Grey-black slippery slime (biofouling) was detected on the bottom. Heterotrophic bacteria, sulphates and sulphides ions were detected in the slime. Corroded surface, rust, mill scale, pits and holes were detected after cleaning from the biofouling (Fig. 9.9). The inner surface of the shell (especially welds) at the height of 2 m from the bottom also was corroded.

Cause of failure Severe corrosion occurred because of appearance of water in kerosene and microorganisms' proliferation. Water appeared in kerosene during wet treating of kerosene at the kerosene treatment unit at the oil refinery.

Results of physico-chemical and microbiological analysis of kerosene, drainage water and sludge formed at the bottom of the kerosene AST are shown in Tables 9.1, 9.2 and 9.3.

The presence of sulphur-containing compounds in kerosene causes its deterioration and as a result copper strip test shows corrosiveness of kerosene (see Table 9.1). It is important to emphasize that there are no standards or limits on most

Table 9.1 Physico-chemical analysis of kerosene in the AST

Parameter	Sulphur (total)	Sulphur (mercaptans)	H ₂ S	Copper strip corrosion test ^a
Value, ppm	220–800	4–86	1	0–2

^a Quality value according to ASTM D130-12, Standard test method for corrosiveness to copper from petroleum products by copper strip test, Book of Standards, vol. 05.01, ASTM International, USA, 2012, p 10

Table 9.2 Physico-chemical analysis of drainage water in the kerosene AST (average during a year)

Parameter	Value
pH	6.4–8.2
Conductivity, $\mu\text{S}/\text{cm}$	26,600–183,000
Cl ⁻ , ppm	24–65,320
SO ₄ ⁻² , ppm	26–700
S ²⁻ , ppm	0.02–0.2
Fe, ppm	0.4–6.5
TBC, bact/ml	0–1,000
SRB, bact/ml	6–10
Organic carbon, mg C/liter	75–1,100
Detergents, ppm	1–2

TBC Total bacteria count, SRB Sulphate reducing bacteria

Table 9.3 Microbiological analysis of sludge in the kerosene AST after a year of service

TBC	SRB	Iron bacteria	Fungi	<i>Thiobacillus thiooxidans</i>
5×10^6	10	4.18×10^6	2.1×10^7	3×10^2

Microorganisms are measured in CFU (colony forming units—amount of microorganisms in 1 ml of sludge)

of parameters of drainage water, but trends in some of them can show possible microbiological deterioration and corrosion occurring in the kerosene AST.

Table 9.2 shows that concentration changes of Cl⁻, SO₄²⁻, TBC and SRB amounts can occur during several months of kerosene storage in the AST. Concentrations of sulphates and chlorides were enough for SRB proliferation. For instance, for propagation *Desulfovibrio salixigens* (one of SRB strains) 2.5 % NaCl and pH = 6.4–8.2 are needed. Kerosene was treated by sodium chloride (NaCl) aqueous solution at kerosene unit at the oil refinery. Certainly this solution often was swept away with kerosene and accumulated in the AST. Concentration of organic carbon (food for microorganisms) in drainage water was enough for the proliferation of microorganisms. Viscous sludge consisted of corrosion products of iron (60 wt%), organic substances including microorganisms (26 wt%), and water (14 wt%). Diverse mi-

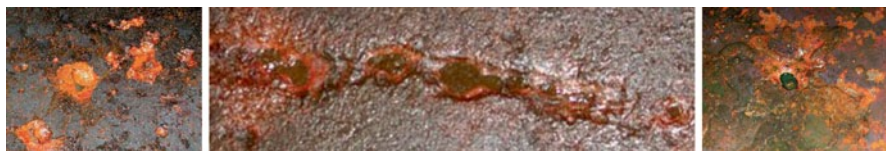


Fig. 9.10 Pits and holes as a result of MIC on the inner surface of the bottom in the AST containing gas oil after 45 years of service

croorganisms were present in sludge (see Table 9.3). Bacteria that were present in sludge could travel into kerosene and contaminate it. In such cases, injection of biocides could help and tank must be immediately cleaned. In any case, kerosene tanks must be drain at least once a week and must be cleaned every 4–5 years. It is recommended also to examine NO_3^- , PO_4^{3-} , Na^+ , K^+ , Ca^{2+} , Mg^{2+} , and redox potential in drainage water.

Solution Periodical drainage, cleaning and coating performance (see Sect. 7).

9.1.9 Case 9. Corrosion of Inner Surface of the Bottom of AST Containing Gas Oil

The AST containing gas oil was in service 45 years. Heterotrophic bacteria were detected in the slime. Rust, shallow pits and holes of dimensions of 10–70 mm were detected at the bottom (Fig. 9.10). Most holes were formed near the welds.

Cause of failure Microbiological analysis and surface morphology of bottom with pits showed occurrence of MIC.

Solution It is not recommended to repair the bottom, namely, to use “patches” for prolongation of service life of bottom as they cause metallurgical and electrochemical heterogeneity of surface. It is recommended to use secondary containment (see Sect. 7.8), and painting (see Appendix L). It is recommended also drainage once a week, examine the presence of microorganisms every month and inspect inner surface of AST every 10–20 years (see Table 8.1).

9.1.10 Case 10. Underground Storage Tank (UST) containing LPG

The carbon steel UST containing LPG was in service 20 years. Visual examination showed formation of red rust (ferric hydroxides and oxides) on the inner surfaces contacted liquid phase (3 m of the height) and black-red corrosion products (mixture of iron sulphide and ferric hydroxides and oxides) on the inner surfaces contacted vapor phase (above 3 m of the height) (Fig. 9.11). Similar corrosion products were formed on pipes located inside this UST containing LPG (Fig. 9.12).



Fig. 9.11 **a** General view of the UST containing LPG. **b** Inner surface contacted liquid phase. **c–e** Inner surface contacted vapor phase. **e** Magnification of **d**



Fig. 9.12 The corroded pipe in the UST containing LPG

Cause of failure The presence of water in LPG caused corrosion of inner surface of the UST shell contacting liquid phase. The presence of water vapor and H_2S in gaseous phase resulted in corrosion of inner surface of the UST shell contacting vapor phase. Iron sulphide is cathodic to carbon steel and in the presence of water condensate pits were formed under black iron sulphides (see Fig. 9.11e). Usually LPG is produced in different units at oil refineries, and this product can contain small amounts of water, hydrogen sulphide and other sulphur containing compounds, and even chlorides. Corrosion rate of carbon steel in drain water from the UST containing LPG was 0.07 mm/year. This is relatively high value for tanks containing petroleum products.

Solution Application of epoxy coating of 550–600 μm thickness (see Appendix L) and VCI use for protection of inner surface contacting vapor phase (see Sect. 7.4).

Recommended Literature

1. ANSI/API RP 575 (2005) Guidelines and methods for inspection of existing atmospheric and low-pressure storage tanks, 2nd edn. American Petroleum Institute, Washington, D.C., p 60

Chapter 10

History of Crude Oil and Petroleum Products

Time is a space for development of abilities.

Karl Marx (1818–1873), a German philosopher.

Abstract Petroleum is an old name of crude oil as consists of two Latin words: *petra* (rock or stone) + *oleum* (oil). Etymology of petroleum products and their use in mankind history is described. Interesting facts in use of naphtha, gasoline, history of anti-knock additives to gasoline, kerosene, diesel fuel, fuel oil and asphalt also are described. Even it is noted how the expression “it smells like kerosene” appeared. It is shown that all history of mankind is related to petroleum products.

Petroleum is an old name of *crude oil* as consists of two Latin words: *petra* (rock or stone) + *oleum* (oil). The term *petroleum* was used in the treatise *De Natura Fossilium*, published in 1556 by the German mineralogist Georg Bauer, also known as Georgius Agricola. *Crude oil* is named also *rock oil* or *mineral oil*. The Latin word ‘*oleum*’ came from the Greek ‘*olive oil*’ and that from ‘*olive tree*’. Crude oil originates from ancient fossilized organic materials, such as zooplankton and algae, which geochemical processes convert into oil. *Crude oil* got the name a *mineral oil* because it does not have an organic origin on human timescales, but is instead obtained from rocks, underground traps, or sands. *Mineral oil* also refers to several specific distillates of crude oil. Thus the name *mineral oil* by itself is imprecise.

The Chinese using bamboo pipes drilled the oil well in 327–347 AD to a depth of 240 m below the ground surface, extract the first drops of oil and called it ‘*shi you*’ which means *rock oil*. This oil was used for the evaporation of sea water and salt production. Crude oil was known as “burning water” in Japan in the seventh century. The deposits of crude oil are located at a depth of tens meters to 5–6 km.

Humans have been using petroleum products for a long time. Asphalt was used in ancient Babylon as mortar for buildings and for waterproofing ships. The bitumen was first used in the eighth century Baghdad to pave roads. Crude oil was distilled by the Persian alchemist Razi in the ninth century producing kerosene which was mainly used for lamps. During the reign of the Byzantine Empire, ‘Greek fire’—an incendiary weapon which exact formula was long lost to history but thought to contain various petroleum products—was a formidable weapon because pouring water on it only intensified its flame. Persian chemists also distilled crude oil in order to

produce flammable products for military purposes. Through Islamic Spain, distillation became available in Western Europe by the twelfth century.

The richest crude oil fields are located in Saudi Arabia, USA, Canada, Russia (Siberia), Iran, and China. Offshore drilling started in the Caspian Sea (near Baku, Azerbaijan) in 1846. In America continent, the first commercial oil well entered operation in Oil Springs (Ontario, Canada) in 1858, while the first offshore oil well was drilled in 1896 on the California Coast.

Nowadays only a half of output crude oil is converted into petroleum products using as fuels, and the other half is involved in the transformation to different chemicals which are used for production of polymers, perfume, toothpaste, detergents, antiseptics, medicines, fertilizers, candles, toys, etc. Crude oil is the source of producing of different petroleum products and their short history is described below.

Naphtha The word *naphtha* came from Latin and Greek where it derived from Persian. It appears in Arabic as *naft* (crude oil) and in Hebrew as *neft*. Even now people use the term *neft* for designation of *kerosene* that is used in heaters. The word *naphtha* was used to refer to any sort of crude oil or pitch. The word *naphtha* is referred to a miraculous flammable liquid in the Old Testament. Naphtha is used primarily as feedstock for producing high octane gasoline (called reformat), in the bitumen mining industry as a diluent, in the petrochemical industry for producing polyethylene and polypropylene, as solvent for cleaning applications, and as a fuel in camp stoves.

Gasoline The word ‘gasolene’ was coined in 1865 from the word *gas* and the chemical suffix *-ine/-ene*. The modern spelling ‘gasoline’ was first used as a brand name for the relatively new petroleum distillate in 1871 (it wasn’t really a motor fuel just yet). Gasoline was actually a brand in the same way that ‘vaseline’ is a brand name for petroleum jelly. And while ‘gasoline’ as a word was never officially registered as a trademark, it isn’t really a gas; it’s a liquid at ambient conditions. It was called ‘gasoline’ because it could vaporize so easily. Some people in the oil industry hoped that it would be used by the coal gas systems being built in most towns. However, though the gasoline was highly volatile it condensed to a liquid too easily, which caused problems in gas systems. Gasoline was initially used as a topical medicinal to rid folks of head lice.

The word ‘petrol’ was first used in reference to the refined substance in 1892 (it was previously used to refer to unrefined petroleum). The shortened form ‘gas’ for ‘gasoline’ was first recorded in American English in 1905 and is often confused with the older word ‘gas’ (‘chaos’ from the Greek) that has been used by the medieval alchemist Paracelsus since the early 1600s.

In the early days of the oil industry, kerosene was the premium product and gasoline was a troublesome byproduct of petroleum refineries. Sometimes it was burned off or just dumped on a field or down a river.

It wasn’t until 1892 with the invention of the automobile that gasoline was recognized as a valuable fuel. Automotive inventors in the late 1800s saw this easy vaporization as a definite advantage because what they wanted was a liquid fuel that could provide an explosive air-fuel mixture for the internal combustion engine.

Since the engines first used to power flight were based on the automotive engines of the day, they were fueled with *automotive gasoline*. *Aviation gasoline* (*avgas*) is gasoline fuel for spark-ignited reciprocating piston engine aircraft and is not to be

confused with *jet fuel*. Avgas like gasoline is very volatile and is extremely flammable at ambient temperatures. Avgas must be distinguished from *mogas* (*motor gasoline*), which is the everyday used in cars. The use of dye in avgas dates back at least to World War I. Avgas reached its development peak during World War II.

10.1 History of Anti-knock Additives to Gasoline, Kerosene, Diesel fuel, Fuel oil and Asphalt

In the late 1910s and early 1920s, the initial systematic studies of the relationship between engine knocking and fuel quality were conducted in England and in the USA. An American chemist Graham Edgar in 1926 added different amounts of n-heptane (normal heptane) and iso-octane (2,2,4-trimethylpentane) to gasoline, and discovered that the knocking stopped when iso-octane was added. This was the origin of the octane rating scale developed by another American chemist Russell Marker in 1926 (see Sect. 2). Chemists and engineers searched for different compounds (antiknock agents) which could increase octane number of gasoline. An American mechanical engineer Thomas Midgley defined in 1921 that injection of small amounts of tetraethyl lead [TEL— $(\text{C}_2\text{H}_5)_4\text{Pb}$] (150 mg Pb/l gasoline) into gasoline eliminated knocking and performed like a higher-octane gasoline. On the one hand, TEL improved anti-knock properties of gasoline. On another hand, harmful properties of TEL use were detected. The TEL was not corrosive to metals but caused formation of deposits in engines and had ecological problems. When gasoline with added TEL was burned in an engine, the lead in TEL was converted to lead oxide which deposited on the valves and spark plugs. These deposits damaged the engine. To avoid deposits of lead oxide inside the engine, lead scavengers were added to the gasoline with TEL. These compounds are volatile and harmful. They are exhausted from the engine along with the rest of the combustion products and deteriorated environment. Lead and its compounds had been recognized since the nineteenth century as dangerous substances which could cause lead poisoning. The Romans did not know this and used lead tubes for drinking water and lead utensils for wine preparation 2,000 years ago. Some historians speculated that lead poisoning was one of the reasons of the declining of the Roman Empire.

Unleaded gasoline was introduced in the 1970s, when the health problems from lead poisoning became apparent. In the United States, leaded gasoline was completely phased out in the 1980s. In European countries leaded gasoline has been forbidden for sale since 2,000 year. TEL was banned for use in motor gasoline in the USA in 1996, but continue to be sold for off-road uses, including aircraft, racing cars, farm equipment, and marine engines.

Scientists have begun searching for unleaded replacement fuels since 1970s and found different oxygenates, aromatics, and organometallic compounds (see Sect. 2). The challenge is daunting because the anti-knock properties of TEL were truly unique. We can compare similar situation with the chromate corrosion inhibitors when it was detected in 1970s that they were toxic. They have been used in cooling water systems with great success since 1930s. Their protective properties

were unique and all new corrosion inhibitors showed lower efficiency. Gradually chromate corrosion inhibitors are changed by less effective compounds. In any case, now the main criterion for choice of use of both fuel additives and corrosion inhibitor is human health and ecology.

Kerosene (paraffin, paraffin oil or coal oil) is a pale yellow or colourless oily liquid with a characteristic odor. The Canadian geologist Abraham Gesner in 1846 produced a clear liquid in distillation of coal tar and oil shale. He showed that this liquid was lamp fuel, and the name *kerosene* was given by him, as a contraction of Greek word *keroselaion* meaning *wax-oil*. However, Abraham Gesner was not the first. The Persian alchemist Razi described in the ninth century two methods of the production of kerosene, termed *white naphtha*. Why kerosene was also called the *paraffin oil*? The Scottish chemist James Young used in 1848 dry distillation of the resinous coal and produced the liquid, which he named the *paraffin oil*, because it congealed at low temperatures into a substance resembling paraffin wax. *Wax* refers to a class of chemical compounds that are plastic (malleable) at ambient temperatures. Wax candles and wax sculptures that we watched in Madame Tussauds museum are typical examples. In history of kerosene production, we also should mention the American Samuel Martin Kier (1813–1874) who was the founder of American petroleum refining industry, and the Polish pharmacist Jan Józef Ignacy Łukasiewicz (1822–1882) residing in Lvov and who built in 1856 probably the first oil refinery in the world. Samuel Martin Kier distilled kerosene by a process of his own invention from crude oil in 1851 and sold it with invented new lamp for the burning of kerosene to local miners under the name *carbon oil*. Ignacy Łukasiewicz distilled kerosene from local seep oil, invented modern kerosene lamp (working with success in local hospital), built the first street lamp in Europe, and constructed the first oil well in Poland. Crude oil became the major source of kerosene after 1859, when Edwin Laurentine Drake (1819–1880) drilled the first oil well in Pennsylvania, USA. It is interesting to note that a Soviet journalist Mikhail Koltsov wrote in 1924 in feuilleton of a major scam (where the most senior U.S. officials were involved) uncovered transmission concessions for the exploitation of oil in California. Here it was first used the expression “it smells like kerosene.”

In my childhood in 1950–1960s, once a week a man and a horse with a harness and two green barrels containing kerosene appeared on our street. A long queue of children and adults with cans lined up. Kerosene was used in lamps for lightning during electricity break and in primus stoves for food preparation. Today kerosene is used as a main aviation fuel. Nevertheless, kerosene is still used as a fuel for heating, cooking, and in lamps. Sometimes it is used as a solvent for greases, as a lubricant, as an effective insecticide, and in the entertainments for fire performances, such as fire breathing, fire juggling or poi, and fire dancing. Illuminating kerosene, producing for lamps, was used to fuel the first turbine engines. Since the engines were thought to be relatively insensitive to fuel properties, kerosene was chosen during World War II mainly because of availability. After the war, the U.S. Air Force started using ‘wide-cut’ fuel representing the mixture of gasoline and kerosene. It was assumed that a wide-cut fuel would be available in larger volumes than either gasoline or kerosene alone. However, compared to kerosene, wide-cut

jet fuel was found to have operational disadvantages: higher volatility; greater risk of fire during handling on the ground; crashes of planes with wide-cut fuel were less survivable. In the 1970s, aircrafts changed back to kerosene. Different types of kerosene are shown in Appendix A (see Table A.9). Wide-cut jet fuel still is used in some northern countries because it is suited to cold climates.

Diesel fuel is a liquid fuel used in diesel engines. The word ‘diesel’ is derived from the family name of the German mechanical engineer Rudolf Christian Karl Diesel (1858–1913) who invented compression-ignition engine in 1892. Rudolf Diesel originally designed the diesel engine to use coal dust as a fuel. He also experimented with some vegetable oils, such as peanut oil (see Sect. 4). Sometimes diesel fuel is called *petroleum diesel* (*petrodiesel*, *fossil diesel* or *diesel oil*).

Fuel oil, named also *black oil*, in some countries is named *mazut*. The word *mazut* was adopted from the Arab word mahzulāt which means ‘wastes, remains’ (after crude oil distillation). The Russian verb ‘мáзать’ (*mazat’*) means ‘to smear’, which means ‘to cover the surface of the object by a fatty substance’. Fuel oil usually is burned directly in boilers and furnaces. Furnaces that burn fuel oil are commonly called ‘waste oil’ heaters or ‘waste oil’ furnaces.

Asphalt (*bitumen*, *asphaltic bitumen*) is not a fuel; it is a residue of crude oil distillation and is used for road surfaces, streets pavement, roofs, and waterproof coating of metals and concrete. It is a black, oily, viscous material that is sometimes a naturally-occurring byproduct of decomposed organic materials. The word *asphalt* is derived from the Greek *ásphaltos* (*ásphalton*) which means ‘asphalt/bitumen/pitch’, which perhaps derives from *á*—‘without’ and *sfallō*—‘make fall’. The word ‘bitumen’ originated in the Sanskrit, where we find the words *jatu*, meaning ‘pitch’, and *jatu-krit*, meaning ‘pitch creating, pitch producing’ (referring to coniferous or resinous trees). ‘Bitumen’ means ‘mining resin’ in Latin.

It was mixed with other materials throughout prehistory and throughout the world for use as a sealant, adhesive, building mortar, incense, and decorative application on pots, buildings, or human skin. The earliest known use of bitumen was by Neanderthals, about 40,000 years ago. The asphalt was used as a water stop between brick walls of a reservoir at Mohenjo-Daro (Pakistan) in 3,000 BC. The material was also useful in waterproofing canoes and other water transport, and in the mummification process toward the end of the New Kingdom (after 1,100 BC) of ancient Egypt. In fact the word from which ‘mummy’ is derived ‘mūmiyyah’ means *bitumen* in Arabic. The primary use of *asphalt* nowadays is in road construction, where it is used as the glue or binder for the aggregate particles. *Asphalt* (*bitumen*) sometimes is confused with *tar* or *coal tar*, which is a similar black thermo-plastic material produced by the destructive distillation of *coal*.

Transportation of crude oils and fuels through pipelines over long distances was developed in the second half of the nineteenth century. Probably the first pipeline made from cast iron and the length of 100 km was built in 1874 for transportation crude oil from the oil field in Pennsylvania to Pittsburg (USA). Then pipeline for transportation crude oil from Baku (Azerbaijan) to Batumi (Georgia) was built in 1894. Pipelines for transportation fuels appeared in 1930s in the USA and Europe.

Really all history of mankind is related to petroleum products.

Recommended Literature

1. Edgar G (1939) Tetraethyllead manufacture and use. *Ind Eng Chem* 31(12):1439–1446
2. Ogston AR (1981) A short history of aviation gasoline development, 1903–1980. Society of Automotive Engineers, paper no. 810848

Appendix

Beware of false knowledge; it is more dangerous than ignorance.
George Bernard Shaw (1856–1950), an Irish playwright

Twelve appendixes contain rich and diverse information about crude oil, petroleum products, fuels, their chemical content, corrosiveness and aggressiveness to metals and polymers; solubility of hydrogen sulphide in organic solvents; water and oxygen solubility in petroleum products, their components, and biofuels; about fuel additives and their purposes; electrical conductivity of petroleum products; chemical composition of some alloys mentioned in the book; standards that should be used for tank design, construction, corrosion control, and inspection; the methodology of experimental study of aboveground storage tanks corrosion; compatibility of polymers with fuels, fuel oxygenates, aromatics, and biofuels; and coating systems for anticorrosion protection of tanks and pipelines.

Appendix A: Physico-Chemical Characteristics and Chemical Composition of Crude Oils and Petroleum Products

A.1 Crude Oil Characteristics

Main characteristic of crude oil is *API* (American Petroleum Institute) *gravity* which shows how heavy or light crude is compared to water (Table A.1).

$$^{\circ}\text{API (or API) gravity} = \frac{141.5}{\text{SG}} - 131.5 \quad (\text{A.1})$$

where API is degrees API gravity; SG is a specific gravity of the crude at 15.56 °C.

The American Petroleum Institute created this scale in 1921. Although mathematically API gravity has no units, it is nevertheless referred to as being in “degrees”. Water has API gravity of 10 (reference). If API gravity of crude is greater than 10, it is lighter and floats on water; if less than 10, it is heavier and sinks. Thus, API gravi-

Table A.1 API gravity, specific gravity and density of crude oils

Degree API	Specific gravity	Density, kg/m ³
8	1.014	1012
9	1.007	1005
10	1.000	998
15	0.966	964
20	0.934	932
25	0.904	902
30	0.876	874
35	0.850	848
40	0.825	823
45	0.802	800
50	0.780	778
55	0.759	757
58	0.747	745

Table A.2 Chemical content of crude oils [1–6]

Element	Weight %
Carbon	80–87
Hydrogen	10–15
Nitrogen	0–2
Oxygen	0–5
Sulphur	0–10
Metals	<0.1

ty is an inverse measure of the relative density of a crude oil and the density of water, and is used to compare the relative densities of crudes. API gravities of most types of crudes range from 12 to 43. Crude oils are classified as *light* (>30 °API; density <870 kg/m³); *intermediate* or *medium* ($20 < \text{°API} < 30$; $870 < \text{density} < 930$ kg/m³); and *heavy* crudes (<20 °API; $930 < \text{density} < 1,000$ kg/m³). Crude oils with API gravity less than 10 °API are referred to as *extra heavy oil* or *bitumen*. For instance, *bitumen* derived from the *oil sands* deposits in the Alberta, Canada area has an API gravity of ~ 8 °API.

Crude oil can be as thin and light-colored as apple cider or as thick and black as melted tar. Thin crudes have relatively low densities and thus high API gravities. Therefore they are called high-gravity crudes. Conversely, thick crudes with relatively high densities are low-gravity crudes. High-gravity crudes contain more of the lighter hydrocarbons and generally have a lower sulphur and nitrogen content, which make it easier to refine.

We should also mention *synthetic crude* and *shale crude*. *Synthetic crude* is an intermediate product produced when *bitumen* (*extra heavy oil*) (or other unconventional oil source) is upgraded into a transportable form. Therefore *synthetic crude* is also named *upgraded crude*. Usually it has ~ 30 °API and is low in sulphur. *Shale oil* (known also as *kerogen oil*) is an unconventional oil produced from *oil shale* by *pyrolysis*, *hydrogenation*, or *thermal dissolution*. *Oil shale* is an organic-rich fine-grained sedimentary rock containing significant amounts of *kerogene* (a solid mixture of organic chemical compounds) from which liquid hydrocarbons called

Table A.3 Physico-chemical characteristics of petroleum products obtained by distillation from crude oils [1]

Petroleum distillate/fuel	Number of C (carbon) atoms	Molecular weight	Distillation range, °C
Gas	C ₁ to C ₄	16 to 58	
Liquefied Petroleum Gas (LPG)	C ₃ to C ₄	42 to 58	–40 to 0
Naphtha	C ₄ to C ₁₂	56 to 170	20 to 210
Gasoline (Motor gasoline)	C ₄ to C ₁₂	56 to 170	20 to 210
Kerosene (Jet fuel)	C ₉ to C ₁₆	128 to 226	150 to 290
Gas oil (diesel fuel, diesel, diesel oil, petrodiesel)	C ₁₂ to C ₂₄	210 to 300	180 to 370
Heating oil (Furnace oil)	C ₁₂ to C ₂₄	210 to 300	180 to 360
Lubricating base oils	C ₂₀ to C ₇₀	>280	340 to 540
Fuel oil (Residual oil)	>C ₂₀	>300	>340
Bitumen (Asphalt)	>C ₄₀	>500	>540
Petroleum coke			Solid

Table A.4 Chemical content (volume %) of the crude oils and petroleum products [1, 3]

Chemical substance	Crude oil wt%	Naphtha	Gasoline	Kerosene (Jet fuel)	Gas oil (Diesel fuel)
Paraffins	15 to 60	65 to 85	30	45	50 to 80
Naphthenes	30 to 60	30	5	35	–
Aromatics	3 to 30	5	up to 35	20	20 to 50
Olefins	–	–	25 ^a	–	–
Asphalts	6	–	–	–	–
MTBE ^b	–	–	up to 15	–	–

^a18% vol. according to EN 228 standard [EN 228:2012. Automotive fuels. Unleaded petrol. Requirements and test methods, 2013, p. 20]

^bIt is the component of gasoline for increase its octane number and better burning

shale oil can be produced. Three processes, *pyrolysis*, *hydrogenation*, and *thermal dissolution*, convert the organic matter within the rock (*kerogene*) into *synthetic oil* and *gas*. Probably you heard about *mineral oil* (see Sect. 10). This name does not mean crude in classic sense. A *mineral oil* is a distillate of crude oil, transparent colorless liquid at standard conditions similar to gasoline. The name *mineral oil* was used by buyers and sellers who did not know and did not understand its chemical content.

A.2 Chemical Compounds in Crude Oils and Petroleum Products

The main chemical compounds occurring in crude oils and petroleum products are hydrocarbons and organic substances containing sulphur, nitrogen and oxygen atoms (Tables A.2, A.3 and A.4).

Hydrocarbons are organic compounds composed entirely of hydrogen and carbon atoms. These atoms are very light (hydrogen is the lightest element in the universe).

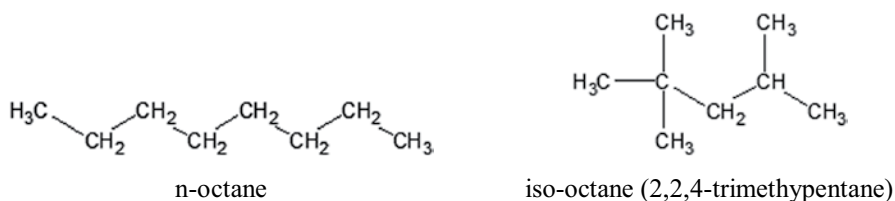


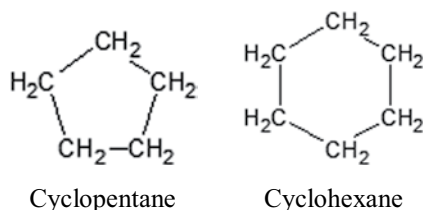
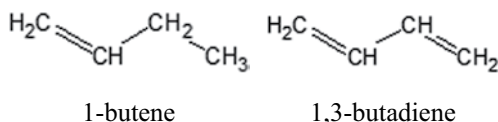
Fig. A.1 Examples of structural isomers of alkanes (paraffins)

There are four major classes of hydrocarbons: alkanes (paraffins), alkenes (olefins), cycloparaffins (naphthens), and aromatics. The members of each class contain different numbers of carbon and hydrogen atoms but share some common structural feature. The classes differ in how the carbon atoms are arranged, i.e., bonded to one another, and in the ratio of hydrogen atoms to carbon atoms. We will describe each of them which are contained in crude oils and petroleum products.

Alkanes (*aliphatic hydrocarbons* or *paraffins*) are types of organic hydrocarbon compounds that have only single chemical bonds between carbon atoms. The word *aliphatic* was derived from the Greek word *aleiphar* meaning 'fat' because it described hydrocarbons derived by chemical degradation of *fats* or *oils*. Alkanes are *saturated hydrocarbons* because no more hydrogen can be added to them without breaking the carbon backbone. Alkanes have the general formula C_nH_{2n+2} , where "n" is the number of carbon atoms; with n ranging from 1 to 40. The first representatives of alkane molecules, from methane (CH_4) to butane (C_4H_{10}), are gases at ambient temperature and pressure. Heavier members of the series, from pentane (C_5H_{12}) to pentadecane ($C_{15}H_{32}$), are liquids. The heaviest molecules of alkanes, from $C_{16}H_{34}$ and more, are solids, called *paraffin wax*. They were identified by German chemist Carl Reichenbach in 1830 who gave the name *paraffin* which means *lacking affinity* or *lacking reactivity*. In the Latin *parum* means *barely* and *affinis* means *affinity*. Alkanes are really stable compounds at ambient conditions. It is possible for alkanes with four and more carbon atoms to have the same number of hydrogen and carbon atoms, but to exist as two or more distinct compounds with different chemical and physical properties. These compounds, called *structural isomers*, differ in the arrangement of the carbon atoms (Fig. A.1).

In *normal alkanes* (*normal paraffins*) the carbon atoms are bonded to form a chainlike zigzag structure. In *iso-alkanes* (*iso-paraffins*) the same carbon atoms form branched structure. Normal octane and iso-octane are two examples of eight-carbon structural isomers C_8H_{18} . Iso-octane is the name for 2,2,4-trimethylpentane; the numbers in the chemical name specify the locations of the three methyl groups (CH_3) attached to the pentane backbone. Hydrocarbons have huge number of isomers. For instance, octane (C_8H_{18}) has 18 isomers. The more number of carbon atoms in hydrocarbons the greater amount of isomers. Alkanes are major constituents of both jet fuel and avgas (aviation gasoline).

Cycloalkanes (*cycloparaffins* or *naphthenes*, not to be confused with naphthalene) are types of saturated hydrocarbons that have one or more rings of carbon atoms in the chemical structure (Fig. A.2).

Fig. A.2 Examples of cycloalkanes (naphthenes)**Fig. A.3** Examples of alkenes (olefins)

Cycloalkanes with a single ring are named analogously to their normal alkane counterpart of the same carbon count: cyclopentane, cyclohexane, etc. Cycloalkanes consist of important minor constituents that have animal or plant precursors and serve as important molecular markers in oil spill and geochemical studies.

Alkenes (*olefins*) are unsaturated hydrocarbons that have at least one double bond between adjacent carbon atoms (Fig. A.3). Dienes (diolefins) contain two double carbon bonds.

Alkenes with one double bond have the general formula C_nH_{2n} (monoalkene). The first representatives of alkene molecules, from ethylene (ethene), C_2H_4 , to butylene (butene), C_4H_8 , are gases at ambient temperature and pressure. With the increase of amounts of carbon atoms a density of alkenes increases and the state of matter changes. Alkenes are rare in nature but can be formed in large amounts during the cracking (breaking down of large hydrocarbon molecules) of crude oils to gasoline in oil refineries' units. Like alkanes, alkenes with four and more carbons can form structural isomers. Propene (C_3H_6) and butene are contained in large amounts in LPG. Alkenes are found in very small amounts in both jet fuel and avgas. Acyclic dialkenes (acyclic olefins or acyclic diens) contain two double bonds, with the general formula C_nH_{2n-2} .

The most prevalent cycloalkenes in crude oils and petroleum products have rings of five and six carbon atoms. Cycloalkenes are major constituents of jet fuels, and found in low concentration in avgas (less than 1%).

Aromatic hydrocarbons (*aromatics*, or *arenes*, or *aryl hydrocarbons*) are hydrocarbons with alternating double and single bonds between carbon atoms (Fig. A.4a, b). The term *aromatic* was assigned before the physical mechanism determining *aromaticity* was discovered, and was derived from the fact that many of the compounds have a sweet scent. As in naphthenes, some of the carbon atoms in aromatics are arranged in a ring, but they are joined by aromatic bonds. Benzene, C_6H_6 , is the simplest aromatic hydrocarbon and was recognized as the first aromatic hydrocarbon with the structure of its bonding suggested by the German chemist Friedrich August Kekulé von Stradonitz in 1865. The configuration of six carbon atoms in aromatic compounds is known as benzene ring where aromatic bond character is distributed evenly around the ring (see Fig. A.4).

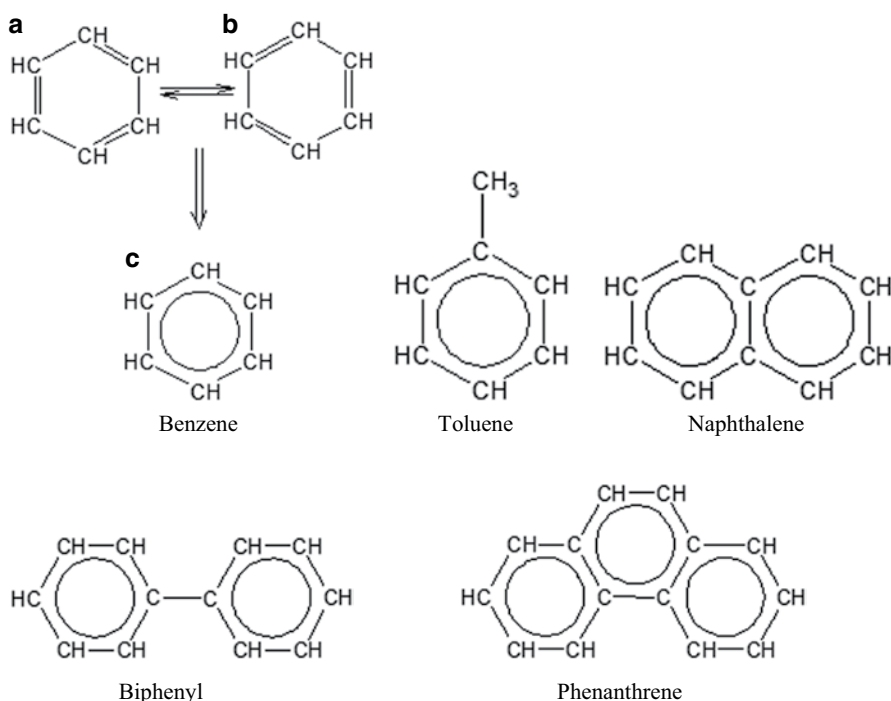


Fig. A.4 Structure of aromatic hydrocarbons. **a**, **b** two equivalent structures of benzene (C_6H_6), **c** shorthand for benzene

The shorthand representation for benzene is a hexagon with an inner circle to represent the aromatic bonds. It is interesting to emphasize those electrons around carbon atoms do not belong to some specific atom but delocalized like in metallic bond. We can call this “collectivization” of electrons in the benzene ring. Aromatic hydrocarbons contain one or more aromatic (benzene) rings connected as fused rings (e.g., naphthalene) or lined rings (e.g., biphenyl) (see Fig. A.4). The ring of one-ring (monocyclic) aromatics like benzene always contains six carbon atoms. In polycyclic aromatics each ring also contains six carbon atoms, but some of the carbon shared by the adjacent rings. Naphthalene is the simplest two-ring (dicyclic) aromatic (see Fig. A.4).

Like olefins, aromatics are unsaturated hydrocarbons. Crude oils contain many aromatic hydrocarbons with alkyl side chains, e.g., mono-, di-, tri-, and tetra-methyl benzenes; naphthalenes; fluorenes; dibenzothiophenes; and phenanthrenes. Toluene and naphthalene are typical aromatic compounds containing in petroleum products. For instance, up to 25% vol. of monocyclic aromatics and to 3% vol. of dicyclic (naphthalene) aromatics are contained in jet fuel. From aromatics only toluene is present in avgas.

Nonhydrocarbon Crude Oil Constituents. They are heteroatomic (*heteros* in Greek means *different, other, or another*) organic compounds and trace metals and can be grouped into six classes: sulphur-, nitrogen-, oxygen- containing compounds, porphyrins, asphaltenes, and trace metals. Sulphur, oxygen and nitrogen are the most common heteroatoms present in crude oils and petroleum products. In spite of sulphur-, oxygen- and nitrogen-containing compounds are present in small amounts, they play a large role in determining certain properties of crude oils and petroleum products, first their corrosivity. All six classes of nonhydrocarbon crude oil constituents will be described below.

Sulphur-containing compounds occurred naturally in all life forms, led to their presence in crude oils, and comprise the most important group of nonhydrocarbon constituents. Composition of sulphur-containing compounds is not less complicated than that of hydrocarbons of petroleum products in which solutions they exist. Among sulphur-containing compounds there are both highly corrosive and not corrosive compounds even corrosion inhibitors, lubricant improvers and antioxidants. The amount of sulphur-containing compounds in petroleum products is low and even in the middle distillates of high sulphur crudes is not more than 5–7 wt%. Sulphur in crude oils and petroleum products can be present as elementary sulphur (S_8), hydrogen sulphide (H_2S) but most sulphur is organically bound. Sulphur atoms form several organic functional groups. The organosulphur compounds consist of thiols, sulphides, polysulphides (disulphides, etc.), cyclic sulphides (e.g., thiophanes and thiophenes). The most prominent groups containing in petroleum products are thiols, sulphides and polysulphides.

- a. *Thiols* are organo-sulphur compounds that contain a carbon-bonded sulphhydryl group ($R-SH$). Thiols are the sulphur analogue of alcohols (for instance, ethanol C_2H_5OH) (that is, sulphur takes the place of oxygen in the hydroxyl group of an alcohol) or phenols. Therefore they are also called thioalcohols and thiophenols. The word *theios* in Greek means *divine* and also *brimstone*. The latter probably is the ancient name for sulphur, because evokes the acrid odor of volcanic activity. Thus, *thion* in Greek means sulphur, and the name *thiol* is the combination of *thio*+*alcohol*. Many thiols have strong odors resembling that of garlic. Thiols are used as odorants to assist in the detection of natural gas (which in pure form is odorless), and the “smell of natural gas” is due to the smell of the thiol used as the odorant (see Sect. 2). Thiols are often referred to as *mercaptans*. The term *mercaptan* is derived from the Latin *mercurium captans* (capturing mercury) because the thiolate group bonds so strongly with mercury compounds. Mercaptans have a sulphur atom bonded to a hydrocarbon group and a hydrogen atom (Fig. A.5 and Table B.1).

Mercaptans possess acidic properties because they have the sulphhydryl ($-SH$) group. Hydrogen in it can be substituted by metal with formation of mercaptides. Corrosivity of mercaptans depends on structure of hydrocarbon radical (R). The less is a radical the greater is corrosivity of mercaptans. Like hydrogen sulphide and sulphur the amount of mercaptans is also restricted in fuels.

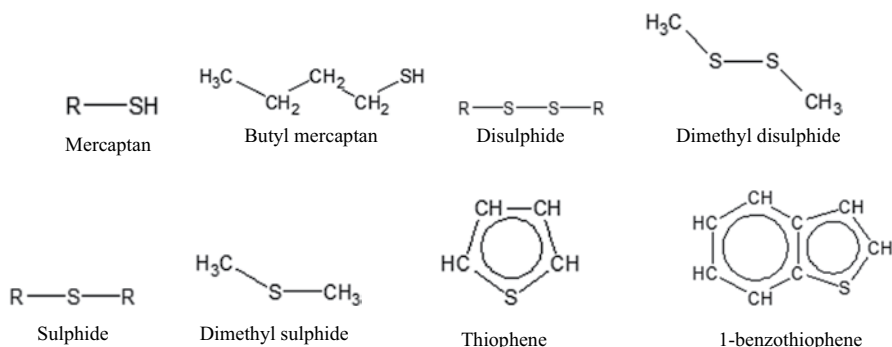


Fig. A.5 Structures of organic sulphur-containing compounds

- b. *Sulphides* are other types of organo-sulphur compounds in which a sulphur atom is bonded to two carbon atoms. Sulphides may be aliphatic ($\text{R}-\text{S}-\text{R}'$) and aromatic ($\text{Ar}-\text{S}-\text{Ar}$). Alkyl cycloalkyl sulphides inhibit corrosion of metals in hydrocarbons. Sulphides are destroyed at high temperatures with formation of H_2S , mercaptans and hydrocarbons.
- c. *Polysulphides* are organo-sulphur compounds containing chains of sulphur atoms bonded together and each also bonded to a hydrocarbon group with the formulae $\text{R}-\text{S}_n-\text{R}'$. Generally compounds with two sulphur atoms bonded together (disulphides) are spread in crude oils and petroleum products. Mercaptans can be oxidized to disulphides. Amounts of disulphides and mercaptans are equal in petroleum products. Mercaptans and disulphides usually occupy not more than 10% of all amounts of sulphur compounds but their negative role in corrosion is huge. When heating disulphides are decomposed like sulphides. Polysulphides can inhibit SCC of carbon and stainless steels. Mono-, di-, and other polysulphides can be used as lubricity improvers.
- d. *Cyclic sulphides (thiophenes)* (see Fig. A.5) are heterocyclic compounds in which sulphur is bound in a flat five-membered aromatic ring. Like aromatic hydrocarbons they possess low reactivity. Sulphur atom in the ring is inert, even at high temperatures. Thiophenes and its derivatives occur in crude oils, sometimes in amounts up to 1–3%. They (especially derivatives of benzothiophenes) are most stable among organo-sulphur compounds at high temperatures. *Thiophane* (named also tetrahydrothiophene) is cyclic thioalkane, namely, saturated analog of thiophene. Thiophane is a volatile colorless liquid with an intensely unpleasant odor, therefore is used as an odorant in LPG and natural gas.

All the above mentioned organo-sulphur compounds can be present in crude oils and petroleum products. The amounts of mercaptans in crudes are less than that of sulphides and thiophenes. Organo-sulphur compounds are less stable than hydrocarbons in the solution of which they are—main constituents of crudes and petroleum products. When organic sulphur-containing compounds are treated by hydrogen at the oil refineries, they are reduced to H_2S and hydrocarbons. It is important to emphasize that burning sulphur-laced organic molecules possesses a

health and environmental threat. Burning of fuels containing even small amounts of sulphur cause formation of sulphur oxides (SO_2 and SO_3 , often named SO_x) in atmosphere and increase its corrosivity. In order to remove sulphur from petroleum products, hydrosulfurization (a catalytic chemical process) is used at oil refineries.

Nitrogen Compounds. Crude oils contain organic nitrogen compounds (0–2 wt%) which can be divided into alkali character (pyridine, quinolines, their derivatives, e.g., benzoquinolines; amines and amides) and neutral character (pyrroles, indoles, carbazoles, benzacarbazoles; acridines). Their content is very low in crudes and petroleum products and, like sulphur and oxygen compounds, are main material of resin formation in petroleum products. Like sulphur-containing compounds the distribution of nitrogen-containing compounds in petroleum products is uneven and most amount is present in heavy fractions boiling above 350°C . Predominantly pyridines, quinolines and their derivatives are present in petroleum products. Some of amines, amides, and pyridine posses by inhibitive properties.

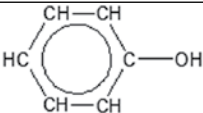

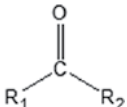
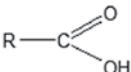
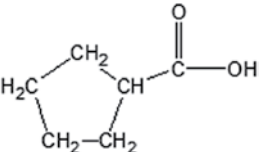
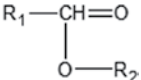
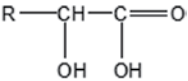
Oxygen-containing compounds in crude oils (0–5 % oxygen) are found primarily in distillation fractions above 190°C and consist of carboxylic acids (including naphthenic acids), and very small amounts of alcohols, phenols, aldehydes, ketones, esters, ethers, and oxyacids (Table A.5). The most part of organic oxygen-containing compounds are molecules possessing large molecular weight and dissolved well in hydrocarbons. The lesser part of oxygen-containing compounds posses low molecular weight and dissolve well in water (carboxylic acids, peroxides and compounds with carbonyl and hydroxyl groups). These low molecular weight carboxylic acids and peroxides are especially corrosive to metals. In addition to the products of oxidation of hydrocarbons in petroleum products, various oxidative products of sulphur- and nitrogen-containing compounds also can be present. Stable oxygen-containing compounds, such as alcohols, ethers and esters, are present in large amounts in petroleum products. Peroxides as the most reactive compounds quickly break up to alcohols, aldehydes and ketones which then turn into acids. Some acids react with alcohols with the formation of ethers. Amount of acids appearing in petroleum products as a result of their auto-oxidation is small comparing to all quantity of oxygen-containing compounds in petroleum products. Phenols are present in crudes and petroleum products in very small amounts, sometimes their quantity is commensurately with that of acids. The quantity of alcohols in kerosene 3–4 times greater than that of phenols. Most amounts of oxygen-containing compounds (alcohols, glycols, ethers) are concentrated in middle distillates (kerosene) and they are relatively stable.

Porphyrins are nitrogen-containing compounds derived from chlorophyll and occur as organo-metallic complexes of vanadium and nickel in crude oils.

Asphaltenes are organic materials consisting of 10–20 fused rings with aliphatic and naphthenic side chains and N-, S-, O-containing compounds. Crude oils can contain up to 20% asphaltenes.

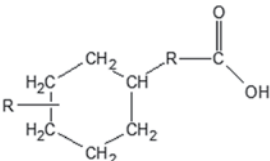
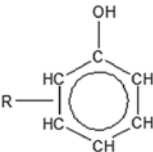
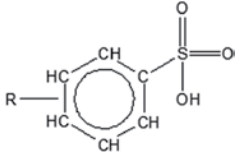
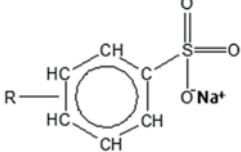
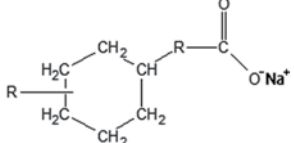
Metals and other inorganic compounds. Vanadium and nickel are the most abundant metallic constituents of crude oils, usually 2–30 ppm, sometimes reaching

Table A.5 Oxygen-containing compounds in crude oils and petroleum products

<i>Generic Name</i>	<i>Chemical Structure</i>	<i>Typical Representative</i>
Alcohol	$R - OH$	C_2H_5OH
Phenol		C_6H_5OH
Aldehydes		$CH_3-CH=O$
Ketones		$CH_3-C(CH_3)=O$
Carboxylic Aliphatic Acids		CH_3COOH
Carboxylic Naphthenic Acids		C_5H_9COOH
Ether	R_1-O-R_2	CH_3-O-CH_3
Ester		$CH_3-C(=O)-O-C_2H_5$
Hydroperoxides	$R-O-OH$	CH_3-O-OH
Peroxide	$R_1-O-O-R_2$	$CH_3-O-O-CH_3$
Oxyacids		$CH_3-CH(OH)-C(=O)OH$

hundreds and even thousands ppm. They are present primarily in porphyrin complexes and other organic compounds. Iron and copper ions can appear as a result of corrosion and can combine with organic acids, mercaptans, disulphides, and phenols. The greater the organic radical, the larger the solubility of such metallo-organic complex in petroleum product. In addition to these complexes, oxides and sulphides of metals can appear in petroleum products as a result of reaction with dissolved oxygen, sulphur and H_2S . Soil dust containing inorganic salts, silt, sand (SiO_2) and metals' oxides also can be present in petroleum products.

Table A.6 Surfactants found in crude oils and fuels

<i>Name</i>	<i>Chemical Structure</i>
Naphthenic acids	
Phenols	
Sulphonic acids	
Sulphonates	
Sodium naphthenates	

R (radical) represents a hydrocarbon group C_nH_m that is a part of the molecule.

Surfactants found in crude oils and petroleum products are shown in Table A.6. They play essential role in formation and stabilization of an undesirable haze and fuel-water emulsions.

A.3 Petroleum Products

Table A.7 The chemical content of kerosene (jet fuel)

Generic type			Amount, % mass	Chemical activity
Name	Example	Formula		
Hydrocarbons				
Paraffins (saturated hydrocarbons; aliphatic):	a) Decane b) 2-methyl-nonane (iso-decane) c) n-dodecane	C_nH_{2n+2} $C_{10}H_{22}$ $C_{10}H_{22}$	33–61	They are chemically inert
a) n-paraffins b) iso-paraffins				
Olefins (unsaturated hydrocarbons)	1-decene	C_nH_{2n} $C_{10}H_{20}$	0.5–5	They are prone to polymerize or oxidize with formation of gums (resins) and deposits
Cycloparaffins (naphthenes; saturated hydrocarbons)	a) Di-ethyl-cyclohexane b) Propyl-cyclohexane	C_nH_{2n} $C_{10}H_{20}$ C_9H_{18}	10–45	They are chemically inert
Aromatics (unsaturated hydrocarbons)	Containing one cycle: a) n-butyl-benzene Containing two cycles: b) Naphthalene	C_nH_{2n-6} $C_{10}H_{14}$ C_nH_{2n-12} $C_{10}H_8$	25 max	Structure is very stable, but coke can be formed during combustion
Sulphur-containing substances				
Mercaptans	Decylthiol	R-SH $C_{10}H_{21}-SH$	20–900 ppm	They improve lubricity; mercaptans increase acidity; deteriorate environment (contaminants and bad odour). $S_{total}=0.4$ wt%
Sulphides	Di-n-butyl-sulphide	R-S-R $C_4H_9-S-C_4H_9$	Not specified	
Di-sulphides	Di-n-butyl-di-sulphide	R-S-S-R $C_4H_9-S-S-C_4H_9$	Not specified	

Physico-chemical properties of kerosene

Density: $d=0.800$ g/cm³ (average)

Distillation range: 150–290 °C

$T_{freezing} \leq -47$ °C (freezing point)

$T_{flash} \geq 38$ °C (flash point)

Table A.8 The physico-chemical properties of chemical components containing in kerosene (jet fuel) (ASTM DS 4B, Physical Constants of Hydrocarbon and Non-Hydrocarbon Compounds, ASTM International, USA, 1991, p. 188)

Hydrocarbon			Boiling Point, °C	Freezing Point, °C	Density at 20 °C, g/cm ³
Name	Formula	Class			
n- Octane	C_8H_{18}	n-Paraffin	125.7	−56.8	0.7027
2-Methylheptane	C_8H_{18}	Isoparaffin	117.6	−109.0	0.6979
1-Methyl-1-ethylcycloheptane	C_8H_{16}	Naphthene	121.5	−143.8	0.7809
Ethylcyclohexane	C_8H_{16}	Naphthene	131.8	−111.3	0.7879
o-Xylene	C_8H_{10}	Aromatic	144.4	−25.2	0.8801

Table A.8 (continued)

Hydrocarbon			Boiling Point, °C	Freezing Point, °C	Density at 20 °C, g/cm ³
Name	Formula	Class			
p-Xylene	C ₈ H ₁₀	Aromatic	138.4	+ 13.3	0.8610
Cis-Decalin	C ₁₀ H ₁₈	Naphthene	195.8	− 43.0	0.8967
Tetralin	C ₁₀ H ₁₂	Aromatic	207.6	− 35.8	0.9695
Naphthalene	C ₁₀ H ₈	Aromatic	217.9	+ 80.3	1.1750
n-Dodecane	C ₁₂ H ₂₆	n-Paraffin	216.3	− 9.6	0.7488
2-Methylundecane	C ₁₂ H ₂₆	Isoparaffin	210.0	− 46.8	0.7458
1-Ethyl-naphthalene	C ₁₂ H ₁₂	Aromatic	258.3	− 13.8	1.0080
n-Nexylbenzene	C ₁₂ H ₁₈	Aromatic	226.1	− 61.0	0.8602
n-Hexadecane	C ₁₆ H ₃₄	n-Paraffin	286.9	+ 18.2	0.7735
2-Methylpentadecane	C ₁₆ H ₃₄	Isoparaffin	281.6	− 7.0	
n-Decylbenzene	C ₁₆ H ₂₆	Aromatic	297.9	− 14.4	0.8554

Table A.9 Jet fuels

US military jet fuel	Year introduced	NATO code	Jet fuel type	Freezing point, °C max	Flash point, °C min	Notes	Joint service designation
JP—1	1944		Kerosene ^a	− 60	43	Obsolete	
JP—2	1945		Wide—cut ^b				
JP—3	1947						
JP—4 ^c	1951	F—40		− 72		US air force fuel	AVTAG/FSII
JP—5 ^d	1952	F—44	Kerosene ^a	− 46	60	US navy fuel	AVTCAT/FSII
JP—6	1956			− 54		Obsolete	
JPTS							
JP—7	1960						
JP—8	1979	F—34					AVTUR/FSII
JP8 + 100	1998						
JP—8 (without FSII)		F—35					AVTUR
JP-9 ^e						Special fuels for aircraft-launched missiles	
JP-10 ^f							

^a Kerosene—a mixture of hydrocarbons each containing 9 to 16 carbon atoms per molecule

^b Wide-cut—a mixture of hydrocarbons each containing 5 to 16 carbon atoms per molecule

^c Jet B—commercial designation; a heavy naphtha-kerosene blend

^d Jet A—commercial designation; used by the world's airlines and US Navy

^e JP-9—a blend of three hydrocarbons: methylcyclohexane, perhydronorbornadiene dimer, and exo-tetrahydrodicyclopentadiene

^f JP-10—essentially a single-hydrocarbon exo-tetrahydrodicyclopentadiene

Table A.10 Six fuel oil grades

Fuel oil grade	Type	Chain length
1	Distillate	9–16
2	Distillate	10–20
3	Distillate	
4	Distillate/Residual	12–70
5	Residual	12–70
6	Residual	20–70

Appendix B: Aggressiveness of Organic Compounds Containing in Crude Oils and Petroleum Products to Metals and Polymers

Chemical compounds that are present in crude oils and petroleum products differently influence corrosion of metals and polymers (Table B.1). Some crude oils inhibit corrosion of carbon steel, even up to 99% water content in crude.

Table B.1 Chemical compounds in crude oil and petroleum products and their aggressiveness to metals, alloys and polymers

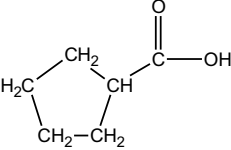
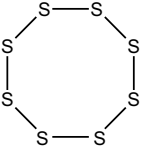
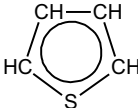
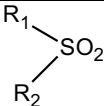
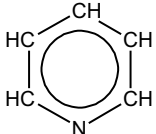
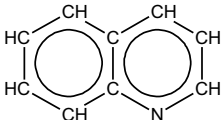
Generic Name		Chemical Formula or Structure	Physical State	Corrosiveness or aggressiveness to	
General name	Typical Representative			metals	polymers and coats
Alkanes (paraffins) (saturated hydrocarbons) C_nH_{2n+2}	Methane, ethane, propane, butane	C_1-C_4	gas	No	No
	Pentane - Heptadecane	$C_5- C_{17}$	liquid		
	Octadecane and more	C_{18} and more	solid		
Alkenes (non-saturated hydrocarbons) C_nH_{2n}	Ethylene, propylene, butylene	C_2-C_4	gas	No	No
	Pentene and more	C_5 and more	liquid		
Cycloalkanes (naphthenes or cyclo-paraffines) (saturated hydrocarbons) C_nH_{2n}	Cyclopentane, Cyclohexane	C_5-C_6	liquid	No	Unknown
Aromatic hydrocarbons (aromatics) C_nH_{2n-6}	Benzene, toluene, xylene	C_6H_6 ; $C_6H_5-CH_3$; $C_6H_4-(CH_3)_2$	liquid	No	Aggressive
Naphthenic Acids $C_nH_{2n-1}COOH$	Cyclopentane carboxylic acid, Cyclohexane carboxylic acid, etc.		liquid	Corrosive at 190 to 360°C	Unknown
Sulphur containing compounds	Sulphur		solid	Depends on temperature and can be corrosive	
	Hydrogen Sulphide	H_2S	gas	Yes	Yes

Table B.1 (continued)

Generic Name		Chemical Formula or Structure	Physical State	Corrosiveness or aggressiveness to	
General name	Typical Representative			metals	polymers and coats
	Mercaptans	R-S-H	gas-liquid ^a	Yes	Unknown
	Sulphides	R ₁ —S—R ₂			
	Disulphides	R ₁ —S—S—R ₂			
	Polysulphides	H ₃ C— $\left[\text{S} \right]_n$ —S—CH ₃	Liquid	Cl ^b	
	Thiophenes				
	Sulphones				
Nitrogen containing compounds	Pyridine		liquid	Cl ^b	Unknown
	Quinoline		liquid		

Note: the matter state of compounds is done for standard conditions (298 K, 1 atm.). R is C_nH_m (hydrocarbon radical).

^aThe state of matter depends on molecular weight.

^bCI - Corrosion Inhibitor.

Appendix C: Solubility of Hydrogen Sulphide in Organic Solvents^a T=293 K

Generic name	Solvent	Chemical formula	Molar weight, g/mol	Solubility	
				Mole fraction ^b	% mass
Alkanes	n-Pentane	C ₅ H ₁₂	72	0.0507	2.460
	n-Hexane	C ₆ H ₁₄	86	0.0537	2.195
	n-Heptane	C ₇ H ₁₆	100	0.0541	1.910
	n-Octane	C ₈ H ₁₈	114	0.0556	1.726
	n-Nonane	C ₉ H ₂₀	128	0.0575	1.595
	n-Decane	C ₁₀ H ₂₂	142	0.0587	1.471
	n-Undecane	C ₁₁ H ₂₄	156	0.0611	1.398
	n-Dodecane	C ₁₂ H ₂₆	170	0.0630	1.327
	n-Tridecane	C ₁₃ H ₂₈	184	0.0655	1.279
	n-Tetradecane	C ₁₄ H ₃₀	198	0.0682	1.241
	n-Pentadecane	C ₁₅ H ₃₂	212	0.0700	1.193
	n-Hexadecane	C ₁₆ H ₃₄	226	0.0708	1.133
Cycloalkanes	Cyclohexane	C ₆ H ₁₂	84	0.0318	1.986
	Decaline	C ₁₀ H ₁₈	138	0.034	0.860
Aromatics	Benzene	C ₆ H ₆	78	0.0561	2.520
	Toluene	C ₇ H ₈	92	0.0663	2.560
	o-Xylene	C ₆ H ₄ (CH ₃) ₂	106	0.0698	2.350
	1-Methylnaphthalene	C ₁₀ H ₇ CH ₃	157	0.0315	0.700
Alcohols	Ethanol	C ₂ H ₅ OH	46	0.0177	1.314
	Ethyleneglycol	C ₂ H ₆ O ₂	62	0.0128	0.940
	n-Pentanol	C ₅ H ₁₁ OH	88	0.0540	2.160
Phenol	Phenol	C ₆ H ₅ OH	94	0.020	0.773
Aromatic alcohols	Benzyl alcohol	C ₆ H ₅ CH ₂ OH	108	0.042	1.400
Hetero-organic compounds	Aniline	C ₆ H ₅ NH ₂	93	0.0610	2.320
	Dimethylaniline	C ₈ H ₁₁ N	121	0.0834	2.493
	Quinoline	C ₉ H ₇ N	129	0.0893	2.520
	Dioxane	C ₄ H ₈ O ₂	88	0.0909	3.726
	Pyridine	C ₅ H ₅ N	79	0.0934	4.246
	Dimethylformamide	(CH ₃) ₂ NCHO	73	0.1382	6.950
	Dimethyl sulphoxide	(CH ₃) ₂ SO	78	0.092	4.230
	Hexametapol (hexamethylphosphoric triamide)	C ₆ H ₁₈ N ₃ OP	179	0.621	23.74
Water	Water	H ₂ O	18	0.0020	0.377

^a Brik SD, Makitra RG, Palchikova EYa (2006) Solubility of hydrogen sulphide in organic solvents. J Inorg Chem 51(3):555–560 (in Russian)

^b Mole fraction = $n(\text{H}_2\text{S}) / [n(\text{H}_2\text{S}) + n(\text{solvent})]$; $n(\text{H}_2\text{S})$ and $n(\text{solvent})$ represent the number of moles of H₂S and solvent, respectively

Appendix D: Solubility of Water in Fuels and their Components

The solubility of water in fuels and their components is given in Tables D.1, D.2 and D.3.

The higher the temperature of the fuel and its components the more dissolved water the fuel can hold. For instance, increase of the temperature from 4 to 43 °C causes twice increase of solubility of water in gasoline. The solubility of water in kerosene at 200 °C thirteen times more than that at 100 °C.

Table D.1 Solubility (ppm) of water in fuels and benzene at 20–25 °C

Fuels and benzene	Gasoline	Naphtha	Kerosene	Diesel fuel	Gas oil	Benzene
Solubility of water, ppm	84	130	30–80	25–150	40–160	582–750

Table D.2 Solubility (ppm) of water in gasoline at different temperatures [7]

T, K	277.55	283.15	288.75	294.25	299.85	305.35	310.95	316.45
Solubility of water, ppm	56	66	75	84	93	104	113	125

Note: Solubility of water given in cm³ /l, was calculated into ppm in [8]

Table D.3 Solubility (ppm) of water in hydrocarbons at different temperatures [5]

Generic name	Hydrocarbon	Chemical formula	Temperature, K					
			273	283	293	303	313	323
Alkanes	n-octane	C ₈ H ₁₈	—	51	95	168	—	—
	2,2,4-trimethylpentane (iso-octane)	C ₈ H ₁₈	31	59	115	201	332	538
	n-hexadecane	C ₁₆ H ₃₄	—	—	69	123	209	332
Cycloalkanes	methyl-cyclo-pentane	C ₆ H ₁₂	—	73	131	205	—	—
	cyclo-hexane	C ₆ H ₁₂	—	67	122	194	317	490
	decaline	C ₁₀ H ₁₈	—	—	63	105	164	—
Alkenes	hexene-1	C ₆ H ₁₂	—	—	—	477	—	—
	cyclo-hexene	C ₆ H ₁₀	—	252	317	424	562	—
Aromatics	benzene	C ₆ H ₆	—	446	582	749	948	1177
	toluene	C ₆ H ₅ -CH ₃	—	316	460	615	750	965
	m-xylene	C ₈ H ₁₀	—	289	402	536	—	—

Appendix E: Solubility of Oxygen in Fuels, Biofuels and their Components

Dissolved oxygen takes part essential role in corrosion and in oxidation of organic compounds containing in fuels and thus increasing corrosivity of fuels and their degradation (see Sect. 1.2 and 5.1). Therefore data about solubility of oxygen in fuels, biofuels and their components are very important. Historically there are many ways of expressing of gas solubility in liquids [9]. Some of them are described below.

The mole fraction (X_g)

$$X_g = \frac{n_g}{n_g + n_{liq}} = \frac{\frac{W_g}{M_g}}{\frac{W_g}{M_g} + \frac{W_{liq}}{M_{liq}}} \quad (E.1)$$

where n_g and n_{liq} are the number of moles of gas and solvent, respectively;

W_g and M_g are the mass (in gram) and molecular mass of gas (32 g/mol for oxygen), respectively; W_{liq} and M_{liq} are the mass (in gram) and molecular mass of solvent (in the case of water, 18 g/mol).

The Bunsen coefficient (α) is defined as the volume of gas absorbed by unit volume of solvent (at the temperature of measurement) under a gas partial pressure of 1 atm.

$$\alpha = \frac{V_g}{V_{liq}} \cdot \frac{273.15}{T}, \left(\frac{cm^3}{cm^3_{liq}} \right) \quad (E.2)$$

where V_g is the volume of gas (oxygen) corrected to 273.15 K and 101,325 Pa (1 atm.) pressure; V_{liq} is the volume of liquid (solvent).

The mole fraction solubility X_g is related to the Bunsen coefficient:

$$X_{g(1 \text{ atm})} = \frac{\alpha}{\alpha + \frac{273.15}{T} \cdot \frac{V_g^o}{V_{liq}^o}} \quad (E.3)$$

where V_g^o and V_{liq}^o are the molar volumes of gas (oxygen) and solvent at a pressure 1 atm.

The Ostwald coefficient (L) is defined as the ratio of the volume of gas (oxygen) absorbed to the volume of the absorbing liquid:

$$L = \frac{V_g}{V_{liq}} \quad (E.4)$$

The Ostwald coefficient L is independent on the partial pressure of the gas (if it is ideal and Henry's Law is applicable). It is necessary, in practice, to state the

temperature and total pressure for which the Ostwald coefficient is measured. Henry's Law describes the influence of pressure on gas (oxygen) solubility in solvents:

$$X_{O_2} = K_H \cdot P_{O_2} \quad (E.5)$$

where K_H is Henry's Law constant; P_{O_2} is the partial pressure of oxygen.

The Ostwald coefficient is related to the Bunsen coefficient by

$$L = \alpha \cdot \frac{T}{273.15} \quad (E.6)$$

The mole fraction solubility, X_{O_2} is related to the Ostwald coefficient by

$$X_{O_2} = \left\{ \frac{RT}{P_{O_2} \cdot L \cdot V_{liq}^o + 1} \right\}^{-1} \quad (E.7)$$

where R is the universal gas constant, $0.082 \frac{l \cdot atm}{mol \cdot K}$; P_{O_2} is the partial pressure of oxygen; V_{liq}^o is the molar volume of solvent. The mole fraction solubility will be at a partial pressure of P_{O_2} .

The weight concentration ppm (*parts per million*) is the amount of milligrams (mg) of solute (oxygen) in 1,000,000 mg (1 kg) of solution. Interconversion of this concentration (ppm), the mole fraction solubility X_{O_2} , and the Ostwald coefficient L are expressed by the Eq. (E.8 and E. 9):

$$ppm = \frac{1,000 \cdot M_{O_2} \cdot X_{O_2}}{M_{liq} \cdot X_{liq}} \quad (E.8)$$

$$ppm = \frac{1,000 \cdot M_{O_2} \cdot \left\{ \frac{RT}{P_{O_2} \cdot L \cdot V_{liq}^o + 1} \right\}^{-1}}{M_{liq} \cdot X_{liq}} \quad (E.9)$$

Most experimental data of oxygen solubility in different solvents were measured in the Ostwald and the Bunsen coefficients, recalculating in some cases into molar fractions X_{O_2} and ppm are given in Tables E.1, E.2, E.3, E.4 and E.5.

Solubility of non-polar oxygen molecules depends on solvent nature, temperature, pressure, and presence of electrolytes. Electrolytes practically do not dissolve in fuels, so only the first three factors are analysed here. Solubility of oxygen in non-polar solvents (fuels and their components) is higher than that in polar solvents (alcohols and water). The heavier is a fuel and hydrocarbons (molar mass) the less solubility of oxygen (see Tables E.1, E.2 and Fig. E.1). It is important to note if the solvent is in equilibrium with pure oxygen at the pressure 1 atm. (101,325 Pa) or with air (at partial oxygen pressure $P_{O_2} = 0.21 \times 101,325 \text{ Pa} = 21,278.25 \text{ Pa}$).

Table E.1 Solubility of oxygen in liquid fuels and petroleum products ($P_{o_2} = 101,325 \text{ Pa}$)

Fuel		Density, g/cm ³	T K	Solubility, L ^a	Reference	
Petroleum ether ^b		0.668	293	0.436	[5]	
				0.438	[10]	
Gasoline ^c	A-93	0.709	293	0.312	[5]	
	A-76			0.273		
	A-72			0.265		
	A-66			0.275		
	100 octane			0.369		[11]
	Lean in olefins			0.334		[10]
	Cracked			0.326		
Kerosene		0.809	293	0.170	[5]	
			273.15	0.220		[11]
			293.15	0.228		
Jet fuel ^c	T-1	0.816	253.15	0.239	[12]	
			273.15	0.228		
			293.15	0.220		
			323.15	0.215		
			293.15	0.236		
	TS-1	0.775	293.15	0.247	[5]	
		0.800		0.241		
				0.184		
	T-2	0.840	253.15	0.184	[12]	
			273.15	0.190		
			293.15	0.212		
			323.15	0.225		
			365.15	0.203		
				0.166		[5]
			0.154	[7]		
Paraffin oil (liquid paraffin)		293	0.159	[10]		
		304.2	0.155	[13]		
		308.2	0.154			
		317.2	0.156			
		330.2	0.163			
		342.2	0.167			
		352.2	0.171			
		363.2	0.174			
	Mineral oil ^d , white	0.8925	297.5	0.146	[14]	
	Oil		A1	293.15	0.124	[15]
			A2	273.15	0.135	
				293.15	0.135	
			333.15	0.145		
			373.15	0.161		
	A3		293.15	0.139		
	A4		293.15	0.139		
	A5		273.15	0.150		
			293.15	0.155		
			333.15	0.164		
			373.15	0.178		

Table E.1 (continued)

Fuel	Density, g/cm ³	T K	Solubility, L ^a	Reference
B1		293.15	0.129	
MK-8 ^c	0.855	293.15	0.163	[12]

^a L is the Ostwald coefficient (see Eq. E.4)

^b Petroleum ether is a petroleum product, named also petroleum naphtha, petroleum spirits or ligroin

^c Gasoline and jet fuels produced in the USSR

^d Petroleum product

^e Aviation lubricating oil produced in the USSR

Table E.2 Solubility of oxygen in organic solvents (components of fuels) at different temperatures [9]

Generic name	Solvent	Chemical formula	T K	Solubility of oxygen in solvents in equilibrium with		
				Pure oxygen	Air	
				($P_{O_2} = 101,325 \text{ Pa}$)	($P_{O_2} = 21,278.25 \text{ Pa}$)	
				$X_{O_2} \cdot 10^3$	ppm	
n-Alkanes	Pentane	C ₅ H ₁₂	298.15	2.05	912	192
			313.15	1.67	743	156
			293.15	1.96	730	153
	Hexane	C ₆ H ₁₄	298.15	1.93	719	151
			313.15	1.52	566	119
			293.15	1.98	634	133
	Heptane	C ₇ H ₁₆	298.15	1.94	621	130
			313.15	1.54	493	103
			283.31	2.16	607	127
	Octane	C ₈ H ₁₈	298.15	2.06	579	126
			298.25	2.05	577	121
			248.15	2.983	839	176
Alkane	Iso-octane (2,2,4-trimethylpentane)	C ₈ H ₁₈	282.87	2.912	819	172
			292.00	2.853	802	168
			298.15	2.814	791	166
			303.36	2.783	783	164
n-Alkanes	Nonane	C ₉ H ₂₀	298.05	2.13	533	111
			298.15	1.99	498	105
			313.15	1.42	355	76
	Decane	C ₁₀ H ₂₂	283.15	2.204	498	105
			298.15	2.025	458	96
			313.15	1.420	320	67
	Undecane	C ₁₁ H ₂₄	298.15	1.82	374	78
			313.15	1.38	283	59
	Dodecane	C ₁₂ H ₂₆	298.15	1.86	350	73
			313.15	1.38	260	55
	Tridecane	C ₁₃ H ₂₈	298.15	1.79	312	65
			313.15	1.39	242	51
	Tetradecane	C ₁₄ H ₃₀	298.15	1.56	252	53
			313.15	1.14	184	39
	Pentadecane	C ₁₅ H ₃₂	298.15	1.72	260	57
			313.15	1.38	209	44
	Hexadecane	C ₁₆ H ₃₄	298.15	1.74	247	52
			313.15	1.38	196	41

Table E.2 (continued)

Generic name	Solvent	Chemical formula	T K	Solubility of oxygen in solvents in equilibrium with		
				Pure oxygen ($P_{O_2} = 101,325 \text{ Pa}$)	Air ($P_{O_2} = 21,278.25 \text{ Pa}$)	
				$X_{O_2} \cdot 10^3$	ppm	
Cycloalkene	Cyclohexene	C_6H_{10}	293.15	1.04	406	85
			298.15	1.04	406	85
Cycloalkane	Cyclohexane	C_6H_{12}	283.47	1.248	476	100
			283.64	1.243	474	99
			284.49	1.239	472	99
			298.15	1.230	469	98
			284.15	1.543	504	106
	Methylcyclohexane	C_7H_{14}	298.24	1.599	522	110
			313.26	1.603	525	110
Aromatics	Benzene	C_6H_6	283.15	0.789	324	68
			288.15	0.795	326	68
			293.15	0.805	330	69
			298.15	0.815	335	70
			303.15	0.821	337	71
			308.15	0.827	339	71
			310.59	0.847	347	73
			323.15	0.857	351	74
			323.15	0.863	354	74
			328.15	0.869	356	75
			333.15	0.879	360	76
			338.15	0.893	366	77
			343.15	0.905	371	78
	Methylbenzene	C_7H_8	293.71	0.922	329	69
			313.20	0.960	334	70
	1,2-Dimethylbenzene	C_8H_{10}	298.15	0.1118	338	71
	1,3-Dimethylbenzene	C_8H_{10}		0.1196	362	76
	1,4-Dimethylbenzene	C_8H_{10}		0.1244	376	79
	Ethylbenzene	C_8H_{10}		0.1220	368	77
	p-Xylene	C_8H_{10}	303.2	0.113	341	72
			323.2	0.114	344	72
			353.2	0.115	347	73
	Propylbenzene	C_9H_{12}	298.15	0.1345	359	75
	Isopropylbenzene	C_9H_{12}		0.1388	370	77
	1-methyl-4-propylbenzene	$C_{10}H_{14}$		0.1429	341	72
	Butylbenzene	$C_{10}H_{14}$		0.1440	344	72
	1-methylpropylbenzene	$C_{10}H_{14}$		0.1569	375	78

Table E.2 (continued)

Generic name	Solvent	Chemical formula	T K	Solubility of oxygen in solvents in equilibrium with		
				Pure oxygen ($P_{O_2} = 101,325 \text{ Pa}$)	Air ($P_{O_2} = 21,278.25 \text{ Pa}$)	
				$X_{O_2} \cdot 10^3$	ppm	
Water		H_2O	273	0.03953	73.80	14.76
			283	0.03072	57.35	11.47
			293	0.02504	46.75	9.35
			298	0.02297	42.75	8.55
			313	0.01870	34.90	6.98
			323	0.01697	31.70	6.34
			333	0.01580	29.50	5.90
			343	0.01507	28.15	5.63
			348	0.01483	27.70	5.54

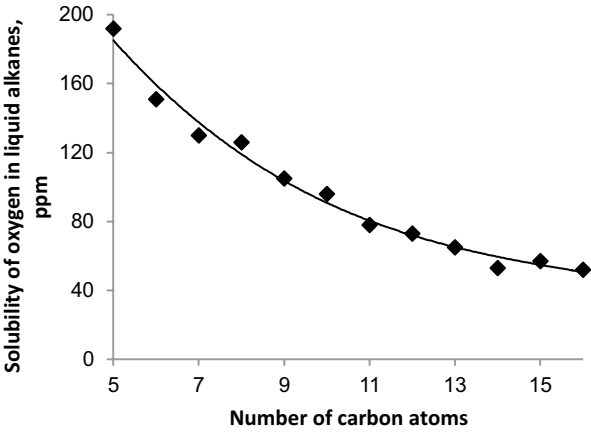


Fig. E.1 Solubility of oxygen in liquid alkanes C_nH_m versus number of carbon atoms, $T = 298 \text{ K}$. Liquid alkanes are in equilibrium with air

Usually increase of temperature causes decrease of oxygen solubility in solvents, but in benzene solubility increases (see Table E.2 and Fig. E.2).

Increase of pressure causes increase of oxygen solubility in solvents (Table E.3).

Solubility of oxygen in biofuels and their components is significantly less than in conventional fuels (Table E.5)

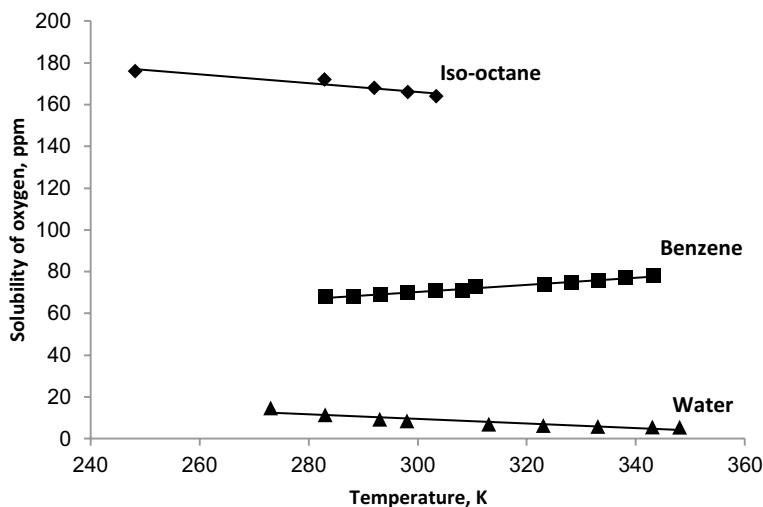


Fig. E.2 Solubility of oxygen in iso-octane, benzene and water versus temperature

Table E.3 Solubility of oxygen in gas oil and pentane at different partial pressure of oxygen, $T = 298\text{ K}$ [7]

P_{O_2} Pa	Gas oil ^a	Pentane ^b	ppm
	L^c	L^c	
13,332	0.020	0.070	19.5
21,331	0.032	0.123	53.8
53,329	0.081	0.304	332.4
101,325	0.154	0.576	119.7

^a Gas oil (density = 0.8762 g/cm^3)

^b Pentane (density = 0.6303 g/cm^3)

^c L is the Ostwald coefficient (see Eq. E.4)

Table E.4 Solubility of oxygen in organic oxygen-containing solvents at 293 K [10]

Solvent	Chemical formula	Solubility of oxygen at (Pa)		
		L ^a	101,325 ^b	21,278.25 ^c
		ppm ^d		
Methanol	CH ₃ OH	0.247	415	87
Ethanol	CH ₃ CH ₂ OH	0.243	413	86
1-propanol	CH ₃ CH ₂ CH ₂ OH	0.214	343	72
2-propanol	CH ₃ CHOHCH ₃	0.247	418	88
1-butanol	CH ₃ (CH ₂) ₃ OH	0.212	348	73
Methyl acetate	CH ₃ COOCH ₃	0.269	384	80
Ethyl acetate	CH ₃ COOCH ₂ CH ₃	0.214	318	67
Diethyl ether	C ₂ H ₅ OC ₂ H ₅	0.450	839	176
Water	H ₂ O	0.033	44	9.2
Ethylene glycol	C ₂ H ₆ O ₂	0.014	16.75	3.5
1,2,3-propanetriol (glycerin)	C ₃ H ₈ O ₃	0.008	8.45	1.8

^a L is the Ostwald coefficient (see Eq. E.4)

^b Partial pressure of oxygen (101,325 Pa)

^c Partial pressure of oxygen (21,278.25 Pa as in the atmosphere)

^d These values (in ppm) are calculated from the Ostwald coefficients L (according to Eq. E.9)

Table E.5 Solubility of oxygen in components of biofuels ($P_{O_2} = 101,325$ Pa)

Solvent		T K	L ^a	Reference
Soybean oil ^b		303	0.156	[15]
		323	0.169	
		343	0.315	
Soybean oil	Raw	295.6	0.173	[16]
	Refined		0.170	
Sunflower seed oil	Raw	295.6	0.151	[16]
	Refined		0.100	
Corn oil		296.15–299.15	0.122	[17]
		318.15	0.127	
Cottonseed oil		296.15–299.15	0.120	[17]
		313.15	0.146	[18]
		318.15	0.126	[17]
Cottonseed oil (hydrogenated)		318.15	0.130	
Castor oil		293	0.162	[10]
Lard (liquid)		313.15	0.132	[18]
		318.15	0.130	[17]
		323	0.114	[19]
Barracudina (fish) oil		293.15	0.099	[20]
		313.15	0.109	
		323.15	0.095	
		353.15	0.075	
Butter oil		313.15	0.163	[18]
		333.15	0.155	
Olive oil		298.5	0.1117	[19]
		298.26	0.1269	[21] ^c
		308.20	0.1312	
		318.53	0.1382	
		327.93	0.1434	
		285.15	0.126	[22]
		298.15	0.130	
		310.15	0.133	
		293.15	0.112	[20] ^d
		313.15	0.126	
		311	0.116	[23]

^a L is the Ostwald coefficient (see Eq. E.4)^b MW=877 g/mol (molecular weight); V^b =960.4 cm³ /mol (molar volume)^c MW=884 g/mol (molecular weight); d=0.9152 g/cm³ (density)^d d=0.9235 and 0.9114 g/cm³ (density) at 293.15 and 313.15 K respectively

Table F.1 (continued)

Additive	Fuel			Purpose	Chemical type of fuel additive	Concentration, ppm	Year of use beginning
	Gasoline	Aviation gasoline	Jet fuel				
Biocides		+	+	Killing microorganisms in fuels and aqueous phase contacting fuels	Substituted dioxaborinanes, isothiazolines and ethylene glycol (injecting into fuels); 2-Bromo-2-nitropropane-1,3-diol ^a ; Glutaraldehyde ^a Tetrahydro-3,5-dimethyl-2H-1,3,5-thiadiazine-2-thione ^a	100–300 25–200 200–5,000 25–200 200–5,000	1950
Cetane improvers				Increase cetane number	Alkyl nitrates; di-tert-butyl peroxide	200–500 100–20,000	1920
Combustion chamber deposit modifiers	+			Prevention or reducing combustion chamber deposits in spark-ignited engines	Organic polyetheramines and compounds containing combination of a saturated carboxylic acid and an alkylated or alkoxylated amine	50–400	1945
Corrosion inhibitors	+	+	+	Prevention or decrease corrosion of metals in contact with fuels	High molecular weight carboxylic acids, aliphatic amines with long chains, the amine salts of carboxylic acids, aliphatic polyamines and polyamides	5–450	1945
Demulsifiers (Dehazers)	+		+	Prevention or removing haze from gasoline and diesel fuel	Alkoxylated polyglycols and aryl sulfonates	3–12	1965
Deposit control additives (dispersants, cleanliness additives)	+		+	Keeping the whole fuel system completely clean and free of extraneous matter (sediment particles, impurities)	Amides, amines, amine carboxylates, polybutene succinimides, polyether amines, polyolefin amines, polymeric methacrylates and derivatives of 2-benzothiazole	10–1,000	1960

Table F.1 (continued)

Additive	Fuel			Purpose	Chemical type of fuel additive	Concentration, ppm	Year of use beginning
	Gasoline	Aviation gasoline	Jet fuel				
Diesel detergency additives (Detergents)							
Diesel fuel stabilizers (Stability improvers)			+	Preventing the formation of deposits (fouling) on the injector nozzle	Succinimide and other ashless polymeric substances	10–200	1980
Drag reducing agents ^b	+			Stabilizing fuel in order to store it for prolonged periods	Long chain and cyclic amines	50–200	1955
			+	Modifying the flow regime by reducing the frictional pressure drop along the pipeline length	Organic high molecular weight polymeric compounds stabilized with aluminum stearate	2–20	1985
Dyes and markers	+	+		Differentiation between various commercial types of fuels	Azo compounds and anthraquinone	2–20	1923
Leak detector additives		+		Detection and location a leak in fuel handling systems	Sulphur hexafluoride (SF ₆)	1	
Lubricity improvers (Anti-wear additives)		+	+	Reducing wear of moving metal surfaces	Carboxylic acids (long chain)	25–1,000	1960
Metal deactivators		+	+	Inhibition catalytic activity of metals (mostly copper and zinc) to oxidize hydrocarbons	Chelating agents (N, N'-disalicyl-dene-1,2-propane diamine)	4–12	1942

Table F.1 (continued)

Additive	Fuel		Purpose		Chemical type of fuel additive	Concentration, ppm	Year of use beginning	
	Gasoline	Aviation gasoline	Jet fuel	Diesel fuel				
Wax anti-settling additives				+	Reducing freezing temperature of diesel fuel (for tanks)	Ethylene vinyl acetate co-polymer (surfactant)	50–1,000	1960
Reodorants				+	To restore, enhance or disguise an odor		250–333	

^a These biocides are injected into aqueous phase contacting fuels
^b Pipeline drag reducing agents. They can be used also in crude oils and fuel oil

Appendix G: Electrical Conductivity of Petroleum Products

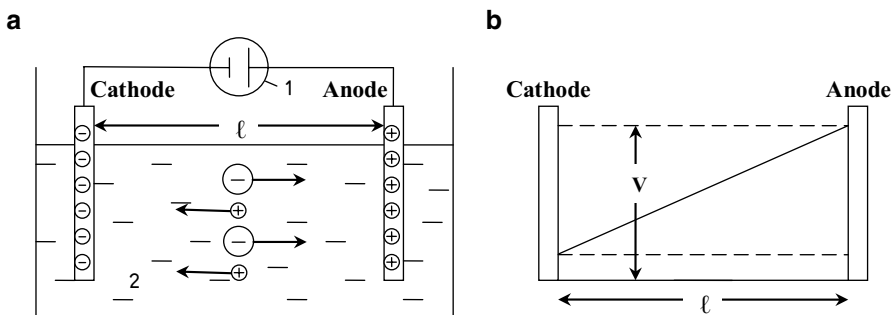


Fig. G.1 The voltage drop V in the electrolyte solution and appearance of electrical resistance R in solution: **a** cell for electrolysis, **b** voltage drop in the cell. 1 source of direct electric current; 2 solution of electrolyte. ℓ the distance between a cathode and an anode

When electrolyte (liquid solution or molten substance containing free ions) is between two electrodes (solution is subjected to voltage drop, or potential difference V between cathode and anode electrodes), free ions rush in the direction of the force thus forming an electric current (Fig. G.1).

An ion is an atom or a group of atoms having charge (cation is a positive and anion is a negative charge).

When liquid contains ions, general positive charge equals to general negative charge.

Cations (\oplus) migrate to negative electrode (cathode) and anions (\ominus) move to positive electrode (anode) in liquid solution. In outer electric circuit electrons move from anode to cathode. Ions do not move in outer electric circuit as well as electrons cannot move in solution. *Electrical conductivity in liquids is the result of directed moving of ions under the gradient of electric potential.* In other words, *electrical conductivity* is a measure of the electric current that a solution carries. *Electrical conductivity* is an estimation of the total concentration of ions in a solution (G.1).

$$\mathbf{i} = \sigma \cdot \mathbf{V} = (\mathbf{n}^+ + \mathbf{n}^-) \cdot \mathbf{q} \cdot \lambda \cdot \mathbf{V} \quad (\text{G.1})$$

where \mathbf{i} is a current density, A/m^2 ; σ is a *specific conductance*, S/m (Siemens/m); \mathbf{V} is a gradient of electric potential, V/m ; \mathbf{n}^+ and \mathbf{n}^- are concentration of positive and negative ions in the volume 1 m^3 ; \mathbf{q} is electric charge of one ion (Coulomb, C) and is defined as the charge transported by a direct (constant) electric current of one ampere (A) in one second ($1\text{C} = 1\text{A} \cdot 1\text{s}$); λ is an ability of moving of ions, $\text{m}^2/(\text{V} \cdot \text{s})$.

It was defined that the law discovered by the German physicist Georg Simon Ohm (1827) for a solid conductor is also applicable for the solutions of electrolytes (G.2).

$$\mathbf{E} = \mathbf{I} \cdot \mathbf{R} \quad (\text{G.2})$$

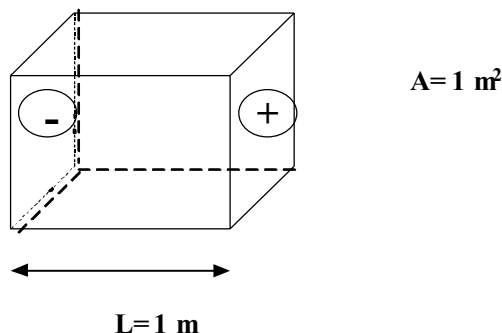


Fig. G.2 Explanation of specific electrical conductivity σ (κ)

E—change of electric potential in solution, Volt; **I**—electric current, Amperes; **R**—electrical resistance of a solution, Ohms.

Electrical resistance **R** of a solution is a reciprocal value of electrical conductivity σ (G.3).

$$R = \rho \cdot \ell / A = [1 / \sigma] \cdot [\ell / A] \quad (\text{G.3})$$

ρ —the specific electrical resistance, Ohm·m (characteristics of conductor, solution in this case); ℓ —the length of the conductor, m (the distance between the electrodes, see Fig. G.1); **A**—a cross-section surface of the conductor, m² (the surface of the electrodes, anode and cathode, in the solution of electrolytes).

We will define the *specific electrical conductivity* σ (sometimes designated by letter κ (kappa) in literature concerning solutions):

$$\sigma = \kappa = 1 / \rho \quad (\text{G.4})$$

Thus σ measures a material's ability to conduct an electric current, namely, is the conductivity of the solution 1 m³ of volume which is situated between two parallel electrodes (anode \oplus and cathode \ominus) of 1 m² area (**A**) on the distance of 1 m (**L**) (Fig. G.2).

Using (G.3) in (G.4),

$$\sigma = (1 / R) \cdot (\ell / A) \quad (\text{G.5})$$

specific electrical conductivity σ is measured in the units Ohm⁻¹ · m⁻¹, or Siemens/m (S/m), where Siemens = 1/Ohm.

$$1\text{ S} = 10^3 \cdot \text{mS} = 10^6 \cdot \mu\text{S} = 10^{12} \cdot \text{pS} \quad (\text{G.6})$$

Table G.1 shows specific electrical conductivity of different liquids.

Liquid petroleum products have very low specific electrical conductivity ($\sim 10^{-12}$ S/m), therefore specific electrical conductivity unit “pS/m” (pico Siemens/meter) named “one conductivity unit” (CU) is used for them.

$$1\text{ CU} = 1\text{ pS/m} = 10^{-12}\text{ S/m} \quad (\text{G.7})$$

Table G.1 Specific electrical conductivity (S/m) of different liquids at 20–25 °C

Liquid	Specific electrical conductivity (S/m), 20 °C	Reference
Sea water	4.8	a
Drinking water	$5 \cdot 10^{-4}$ to $5 \cdot 10^{-2}$	a
Formic acid	$6.4 \cdot 10^{-3}$	a
iso-Propyl alcohol	$3.5 \cdot 10^{-4}$	a
Methanol	10^{-4}	c
Glycol	$3 \cdot 10^{-5}$	a
Ethanol	$2 \cdot 10^{-5}$	c
1-Propanol	10^{-5}	c
Crude oil	10^{-5}	b
iso-Butyl alcohol	$8 \cdot 10^{-6}$	a
1-Butanol	$7 \cdot 10^{-6}$	c
Glycerol	$6.4 \cdot 10^{-6}$	a
Acetone	$6 \cdot 10^{-6}$	a
Deionized water	$4 \cdot 10^{-6}$	a
Ethyl acetate	$4 \cdot 10^{-6}$	c
Benzene	$3 \cdot 10^{-6}$	c
Diethyl ether	$2 \cdot 10^{-6}$	c
Acetic acid	10^{-6}	a
Hexane	$< 10^{-6}$	a
Propionic acid	$< 10^{-7}$	a
Pentane	$< 2 \cdot 10^{-8}$	a
Fuel oil	$2 \cdot 10^{-11}$ to $3 \cdot 10^{-7}$	b
Kerosene	10^{-13} to 10^{-9}	b
Jet fuel	10^{-12} to 10^{-10}	b
Diesel fuel	$(3-5) \cdot 10^{-11}$	b
Avgas	$(1-3) \cdot 10^{-11}$	b
Gasoline	$3 \cdot 10^{-11}$	a
Cyclohexadiene-1,3	$< 6.5 \cdot 10^{-11}$	b
Cyclohexadiene-1,4	$< 5.0 \cdot 10^{-11}$	b
Ethyl ether	$< 4 \cdot 10^{-11}$	a
Cyclohexene	$< 1.5 \cdot 10^{-11}$	b
Cyclohexane	$< 10^{-11}$	b
Heptane	$< 10^{-11}$	a
Toluene	$< 10^{-12}$	a

^a John A. Dean, *Lange's Handbook of Chemistry*, Fifteenth Edition, McGRAW-HILL, INC., New York, USA, 1999, pp. 8.161–8.162

^b Chertkov YaB (1968) Modern and long-term hydrocarbon jet and diesel fuels. Publisher “Chimiya”, Moscow, p 356 (in Russian)

^c Brossia CS, Kelly RG (1995) Organic liquids. Corrosion tests and standards: application and interpretation, Robert Baboian, Editor, ASTM Manual Series: MNL 20, ASTM, USA, p 373

Specific electrical conductivities of petroleum products (10^{-11} S/m for gasoline and kerosene) are million times less than that of crude oil ($\sim 10^{-5}$ S/m), very pure (de-ionized or demineralized) water ($4 \cdot 10^{-6}$ S/m) and such organic liquids as alcohols, ketones, and ethers (10^{-6} – 10^{-5} S/m).

Appendix H: Chemical Composition of Alloys

Table H.1 Chemical composition of aluminum alloys (wt%)

Alloy		Mg	Cu	Mn	Si	Fe	Cr	Other metals	Al
UNS	ASTM								
A91100	Al 1100		0.06						Rem. ^a
A95052	Al 5052	2.2–2.8	<0.1	<0.1	8.0–11.0			(Si+Fe) <0.45	Rem. ^a
A03800	AlSi9Cu3		2.0–4.0	<0.55		0.6–1.1	<0.15		Rem. ^a
	Al6061	0.8–1.2	0.15–0.4	<0.15	0.4–0.8	<0.7	0.04–0.35	Ti <0.15 Zn <0.25	Rem. ^a
	A319	<0.1	3.0–4.0	<0.5	5.5–6.5	<1			Rem. ^a
A03560	A356 (7Si–0.3Mg)	0.20–0.45	<0.25	<0.35	6.5–7.5	<0.6		Ti <0.25 Zn <0.35	Rem. ^a
	A380	<0.3	3.0–4.0	<0.5	7.5–9.5	<1			Rem. ^a
	A384		3.0–4.5		10.5–12	1.1–1.3			Rem. ^a

^a Rem. Remainder

^b A384 T5 heat treated aluminum die-cast alloy

Table H.2 Chemical composition of carbon steels and cast iron (wt%)

Alloy			C	Mn	P	S	Si	Cu	Fe
UNS	AISI/ ASTM	EN ^a							
G10100	C1010		0.10	0.3–0.5	Max 0.04	Max 0.05	0.1	–	Rem. ^b
G10200	C1020		0.20	0.7–1.0	Max 0.04	Max 0.05	0.1	–	Rem. ^b
G10300	C1030		0.27– 0.34	0.60–0.90	Max 0.04	Max 0.05			Rem. ^b
K02700	A516 Grade 70		0.27	0.79–1.30	Max 0.035	Max 0.035	0.13– 0.45	–	Rem. ^b
		S0235JR (St 37)	0.19	1.50	Max 0.045	Max 0.045	–	0.60	Rem. ^b
	CL 30 ^c		3.4	0.5			1.8		Rem. ^b

^a EN European Standard

^b Rem. Remainder

^c Gray cast iron

Table H.3 Chemical composition of stainless steels (wt%)

Alloy		Cr	Ni	C ^a	Mo	Mn ^a	P ^a	S ^a	Si ^a	N ^a	Fe
UNS	AISI										
S30400	304	18–20	8–12	0.08	–	2.0	0.045	0.03	0.75	0.1	Rem. ^b
S30403	304L	18–20	8–12	0.03	–	2.0	0.045	0.03	0.75	0.1	Rem. ^b
S31600	316	16–18	10–14	0.08	2–3	2.0	0.045	0.03	0.75	0.1	Rem. ^b
S31603	316L	16–18	10–14	0.03	2–3	2.0	0.045	0.03	0.75	0.1	Rem. ^b
S31700	317	18–20	11–15	0.08	3–4	2.0	0.045	0.03	0.75	0.1	Rem. ^b
S31703	317L	18–20	11–15	0.03	3–4	2.0	0.045	0.03	0.75	0.1	Rem. ^b
S32100 ^c	321 ^c	17–19	9–12	0.08	–	2.0	0.045	0.03	0.75		Rem. ^b
S44400 ^d	444 ^d	17.5–19.5	1max	0.025	1.75–2.5	1.0	0.04	0.03	1.0	0.035	Rem. ^b

^a Maximum content

^b Rem. Remainder

^c Ti is present in content 5 × C (0.70 max)

^d Ferritic stainless steel. It contains also titanium + columbium [0.20 + 4 × (C + N)min.] – 0.8 wt% max

Table H.4 Chemical composition of duplex stainless steels (wt%)

Alloy	Cr	Ni	C ^a	Mo	Mn ^a	P ^a	S ^a	Si ^a	N	Cu	Fe
UNS	Proprietary designation										
S31803	21–23	4.5–6.5	0.3	2.5–3.5	2.0	0.03	0.02	1	0.08–0.2		Rem. ^b
S32205	22–23	4.5–6.5	0.3	3–3.5	2.0	0.03	0.02	1	0.14–0.2		Rem. ^b
S32003	19.5–22.5	3–4	0.03	1.5–2.0	2.0	0.03	0.02	1	0.14–0.2		Rem. ^b
S32101	21–22	1.35–1.7	0.04	0.1–0.8	4–6			1	0.2–0.25	0.1–0.8	Rem. ^b
S32304	23	4	0.02	0.2			0.001		0.1		Rem. ^b
S32550	24–27	4.5–6.5	0.04	2.9–3.9	1.5			1			Rem. ^b
S32520	24–26	5.5–8	0.03	3–4	1.5	0.035	0.02	0.8	0.02–0.35	0.5–2	Rem. ^b
S32750	24–26	6–8	0.03		1.2	0.035	0.02	0.8	0.24–0.32	0.5	Rem. ^b
S32760 ^c	24–26	6–8	0.03	3–4	1.0	0.03	0.02	1	0.2–0.3	0.5–1	Rem. ^b

^a Maximum content
^b Rem. Remainder
^c Contains tungsten W (0.5–1 wt%)

Table H.5 Chemical composition of copper and brass (wt%)

Alloy		Cu	Zn	Fe	Pb
Name	UNS				
Copper	C11000	≥99.90	–	–	–
Brass ^a	C26800	66	33.86	0.05	0.09

^a Yellow Brass (66% Cu)

Appendix I: Standards for Tank Design, Constructions, Corrosion Control, and Inspection

Standard	Issue	Reference
API 620	Design and construction of large, welded, low-pressure storage tanks	[25]
API 650	Requirements for material, design, fabrication, erection, and testing for vertical, cylindrical, aboveground, closed- and open-top, welded storage tanks in various sizes and capacities with a maximum design temperature exceeding 93 °C	[26]
BS 2654	Manufacture of vertical steel welded non-refrigerated storage tanks with butt-welded shells for the petroleum industry	[27]
DIN 4119	Above-ground cylindrical flat-bottom tank installations of metallic materials; fundamentals, design, tests	[28]
UL 142	Steel aboveground tanks for flammable and combustible liquids	[29]
API Spec 12B	Material, design, and erection requirements for vertical, cylindrical, aboveground, bolted steel tanks (12–1,200 m ³)	[30] [31]
API Spec 12D	Material, design, fabrication, and testing requirements for vertical, cylindrical, aboveground, closed top, welded steel storage tanks (60–1,200 m ³)	[32]
API Spec 12F	Material, design, fabrication, and testing requirements for shop-fabricated vertical, cylindrical, aboveground, closed top, welded steel storage tanks (11–90 m ³)	
API RP 651	Cathodic protection	[33]
API RP 1632		[34]
NACE SP0285		[35]
NACE RP0193		[36]
NACE TM 0101		[37]
STI R051		[38]
STI R972		[39]
API RP 1615	Installation of underground petroleum storage systems	[40]
API RP 652	Interior lining of aboveground storage tanks	[41]
API RP 1631	Interior lining and periodic inspection of underground storage tanks	[42]
UL 1746	External coatings on steel UST (polyurethanes, epoxies, and reinforced plastics)	[43] [44]
STI-P3		[44]
API 653	Tank inspection, repair, alteration and reconstruction	[45]
API RP 575	Frequency and methods of inspection, repair, and preparation of records and reports	[46]
API 510	In-service inspection, rating, repair, and alteration in pressure vessels	[47]
EEMUA 159	Inspection, maintenance and repair of aboveground vertical cylindrical steel storage tanks	[48]
NACE RP0288	Inspection of Linings on Steel and Concrete	[49]
ASTM G 158	Assessing tank integrity, inspection, repairing, and interior lining	[50]
ASTM E 1990		[51]
KWA		[52]
NFPA 326		[53]
NLPA 631		[54]

Standard	Issue	Reference
NFPA 30	Installation of underground liquid storage systems	[55]
PEI/RP100		[56]
API RP 1621 (R2001)	Underground storage of motor fuels and used oil at retail and commercial facilities	[57]
API RP 1595	Design, construction, operation, maintenance, and inspection of aviation pre-airfield storage terminals	[58]
API/IP RP 1540	Design, construction, operation and maintenance of aviation fueling facilities	[59]
API 2610	Design, construction, operation, maintenance, and inspection of terminal and tank facilities	[60]
UL 58	UST and piping	[61]
STI-R922		[62]
API Spec 12P	Fiberglass reinforced plastic tanks	[63]
STI-F894		[64]
STI-F961		[65]
UL 1316		[66]
CAN4–5615-M83		[67]
PEI/RP900	Inspection and maintenance of UST systems	[68]
API RP 1626	Tanks for alcohols and alcohol-gasoline blends	[69]
API RP 1627		[70]
EEMUA 154	Demolition of vertical cylindrical steel storage tanks and storage spheres	[71]

Standard Developing Organizations

API	American Petroleum Institute.
ASTM International	American Society for Testing and Materials.
EEMUA	Engineering Equipment and Materials Users Association.
KWA	Ken Wilcox Associates, Inc.
NACE International	National Association of Corrosion Engineers.
NFPA	National Fire Protection Association.
NLPA	National Leak Prevention Association.
PEI	Petroleum Equipment Institute.
STI	Steel Tank Institute.
UL	Underwriters Laboratories Inc.

Appendix J: The Experimental Study of Aboveground Storage Tanks' Corrosion

Methodology of experimental study of corrosion of inner surfaces of 35 AST (10 gasoline, 4 kerosene, 6 gas oil, 14 fuel oil, and one crude oil), its results are described below and in Sect. 5.8. Volume of these tanks differed from 5,500 to 13,500 m³. The diameter changed from 23.7 to 36.6 m, and the height was 12.8 m. Original thicknesses of the AST were taken from the technical data. They were 10 mm for bottom plates (floors) and 5 mm for roof plates. Original thicknesses of strips changed from 18.26 mm (lower, the 1st strip) to 6.35 mm (upper, the 7th strip) (see Table J.1). Ultrasonic testing was used for measuring of thicknesses of metallic parts of tanks: floors, critical zones occupying 76 mm by perimeter on floors, shell strips, roofs, and pontoons (see Sect. 5.8, Figs. 5.28, 5.29 and 5.30). These measurements were carried out the first time during 55–70 years of the AST service. The average, maximum and acceptable corrosion rates were calculated during this period.

Corrosion rate K of various parts of the AST was calculated according to the formula:

$$K = \frac{D_o - D_i}{t} \quad (J.1)$$

where K is a corrosion rate, mm/year; D_o is original thickness of strips, mm; D_i is measured thickness of strips after t years of service, mm; t is a service period of AST, years.

Statistical data were based on division of tanks' shell strips, roofs and floors on four zones according to geographical direction: south, north, west, and east. This division was done exclusively for convenience of the data treatment.

The results of measurements of thicknesses of different parts of AST and calculated corrosion rates are given for gasoline, kerosene, gas oil, fuel oil and crude oil (typical examples for each fuel) AST in Table J.1 and analysed in Sect. 5.8. The minimum acceptable thicknesses of various AST parts were calculated according to the standard API 653 [45]:

$$t_{\min} = \frac{2.6 \cdot D \cdot (H - 1) \cdot G}{S \cdot E} \quad (J.2)$$

where t_{\min} is the minimum acceptable thickness, inches (1 inch = 2.54 cm); D is diameter of tank, feet (1 foot = 30.48 cm); H is height of tank from the bottom to the maximum design liquid level, feet; G is the highest specific gravity of liquid containing in tank; S is maximum allowable stress, pounds per square inch (1 pound = 0.454 kg), use the smaller of 0.8Y or 0.426 T for bottom and second strip, use the smaller of 0.88Y or 0.472T for all other strips; Y is the minimum yield strength of the plate (use 30,000 pounds per square inch if not known); T is the smaller of the minimum tensile strength of the plate (use 55,000 pounds per square inch if not known); E is original joint efficiency for the tank (use 0.7 if E is unknown).

These calculated values (t_{\min}) also are given in Table J.1.

Table J.1 Results for gasoline AST (south, example after 65 years of service)

Strip	Thickness, mm			Corrosion rate, mm/year			
	Original	Current	Average	Minimum acceptable by API 653	Max	Average	Acceptable
		(minimum) After 65 years					
7	6.35	5.50	5.70	2.54	0.013	0.010	0.059
6	6.35	3.00	4.10	3.59	0.052	0.040	0.042
5	9.53	2.60	4.20	5.55	0.110	0.082	0.061
4	10.32	4.20	4.40	7.51	0.094	0.091	0.043
3	12.70	6.20	7.40	9.47	0.100	0.082	0.050
2	15.88	10.60	10.60	12.59	0.081	0.081	0.050
1	18.26	17.60	18.10	14.16	0.010	0.002	0.063

Note: The thickness gauge 26DL of “Panametrics” with the accuracy ± 0.01 mm was used

Table J.2 Corrosion rates (mm/year) of inner surfaces of different parts of AST containing crude oil and petroleum products

Media	Part of AST	Corrosion Rates, mm/year		Reference
		Uniform corrosion	Pitting	
Crude oil	Roof	0.1–0.5	0.5–5.0	[72]
	Bottom	0.05–0.5	0.4–5.0	[73, 74]
		0.32		[75, 76]
	Roof and Upper Strip	1.5		[77, 78]
Gasoline	Bottom and Lower Strip	1.0	2–5	[77, 78]
	Shell	0.04–0.13		[75, 76, 79]
		0.15 ^a		[80]
		0.375 ^b		
Naphtha		0.12–0.50		[7, 81]
	Shell	0.016–0.047		[76, 79]
	Bottom	0.062		
	Critical zone (bottom)	0.087		
Kerosene and gas oil service	Shell	0.04		[7, 81]
Kerosene	Shell	0.017–0.040		[76, 79]
	Bottom	0.005–0.025; 0.024–0.105		
Gas oil	Roof		1.0	[75, 76, 82]
	Bottom		0.5	
	Shell	0.01–0.05		[76, 79]
	Beam (upper part)	0.04–0.07		
Fuel oil	Shell	0.006–0.014		[75, 76]
	Roof	0.3		[82, 83]
		0.5		[79]
	Bottom	0.3–0.4 (outer surface)		[82, 84]

^a Industrial region Northeastern USA

^b Near the ocean Southeast Gulf Coast USA

Corrosion rates of different parts of AST containing crude oil and petroleum products from different sources are summarized in Table J.2.

Appendix K: Compatibility of Polymers With Liquid Fuels, Fuel oxygenates, Aromatics, and Biofuels

Table K.1 Designation and chemical type of elastomers [85–91]

Designation	Elastomer type
ACM	Polyacrylate (acrylic, polyacrylic, ethylene acrylic)
AU, U	Polyester urethane
BR	Polybutadiene
CIIR	Chlorine isobutylene-isoprene rubber (Butyl rubber, Neoprene rubber)
CO, ECO	Epichlorohydrin rubber (epichlorohydrin homopolymer)
CPE	Chlorinated polyethylene
CR	Polychloroprene
CSM	Chlorosulphonated polyethylene (Hypalon)
CSPE	Chlorosulphonated polyethylene
EPDM	Ethylene propylene diene monomer (terpolymer)
EPM	Ethylene propylenecopolymer
FKM ^a	Fluoroelastomer (Viton)—Fluorocarbon rubber
FMQ, FSI	Fluorosilicone
HDPE	High density polyethylene
HNBR	Hydrogenated nitrile rubber (peroxide cured)
IIR	Isobutylene-isoprene ('Butyl')
IR	Polyisoprene (high vinyl)
NBR	Nitrile butadiene rubber (Buna-N; Nitrile; Butadiene-acrylonitrile)
NBR (H)	Butadiene-acrylonitrile ('Nitrile') (> 36 % ACN ^b)
NBR (M)	Butadiene-acrylonitrile (25–36 % ACN)
NBR (L)	Butadiene-acrylonitrile (<25 % ACN)
NBR-BIIR	Nitrile butadiene rubber—Bromo butyl rubber
NBR-CSM	Nitrile butadiene rubber—Chlorosulphonated polyethylene
NBR-CR	Nitrile-polychloroprene blend (nitrile the major component)
NBR-PVC	Nitrile-polyvinylchloride blend (50/50)
NR	Natural rubber
PA	Polyamide
PS	Polystyrene
SI	Silicone

^a FKM is the name of fluoroelastomer (Viton) according to ASTM D1418 [85]. FPM is the name of the same fluoroelastomer according to ISO 1629

^b Acrylonitrile

Table K.2 Resistance of Viton (fluoroelastomers) to liquid fuels and solvents

Media	Type of Viton ^a							
	A	B	F	GB	GF	GLT	GFLT	ETP
	Cure System							
	Bisphenol			Peroxide				
Aliphatic hydrocarbons	E	E	E	E	E	E	E	E
Aromatics	G	E	E	E	E	G	E	E
Automotive and aviation fuels	E	E	E	E	E	E	E	E
Gasoline containing 5 to 15% vol. of alcohols and ethers (methanol, ethanol, MTBE, TAME)	G	E	E	E	E	G	E	E
Gasoline/methanol fuel blends (up to 100% vol. methanol)	NR	G	E	G	E	NR	E	E
MTBE	NR	NR	NR	NR	NR	NR	NR	E—G
Strong alkali and amines	NR	NR	NR	NR	NR	NR	NR	E—G
Swelling (% vol.) in methanol	75–105	35–45	5–10	65	5–10	75–105	5–10	low

Notes: *E* Excellent (minimum volume swell); *G* Very good (small volume swell); *NR* Not Recommended (excessive volume swell or change in physical properties)

^a *Viton* is a brand of synthetic rubber and fluoroelastomer commonly used in O-rings, gaskets and seals. The fluorine content of Viton polymers varies between 66 and 70%

Fluoroelastomers can be divided into different classes on the basis of their chemical composition, fluorine content or crosslinking mechanism.

Viton A—66% fluorine; Viton B—68% fluorine; Viton F—70% fluorine; Viton GF—70% fluorine; Viton GLT—64% fluorine; Viton GFLT—66.5% fluorine; Viton ETP—67% fluorine.

Table K.3 Compatibility of polymers to the model fuel ethanol E10 and E20 [89]

Compatible	Non-compatible
PA 6 (Polyamide—Nylon 6)	ABS (Acrylonitrile Butadiene Styrene)
PA 66 (Polyamide—Nylon 66)	PUR (Polyurethane nonrigid, soft)
PET (Polyethylene Terephthalate—Mylar)	PVC (Polyvinyl Chloride)
PEI (Polyetherimide -GE Ultem)	PBT (Polybutylene Terephthalate)

Notes: ASTM Fuel C: 50% iso-octane + 50% toluene

E10—90% Fuel C + 10% aggressive ethanol

E20—80% Fuel C + 20% aggressive ethanol

Aggressive ethanol consists of the mixture synthetic ethanol (816.00 g), de-ionized water (8.103 g), sodium chloride (0.004 g), sulfuric acid (0.021 g), and glacial acetic acid (0.061 g).

Specimens were immersed for 3,024 h at 55°C according to ASTM D543 [88].

Table K.4 Swelling of polymers and fiberglass in model fuels with and without oxygenates [89]

Polymer	Application	Swelling, % vol.			
		ASTM FuelC ^a	ASTM FuelC + MTBE (15 % vol.)	ASTM FuelC + CH ₃ OH (10–15 % vol.)	ASTM FuelC + C ₂ H ₅ OH (10–15 % vol.)
NBR	Hose	23–56; 28 ^b	19–38	49 ^b –106	22–70; 34 ^b
FKM	Seal	1–14; 10 ^b	6–18 ^b	7–46 ^b	6–24
FSI	Seal	18–21	24	30	20
CO, ECO		35–40		77–80	50–65
U	Seal	21	24	58	51
CSPE		61		66	81
CIIR		96		81	
CPE				87	
PS	Sealant	27		28	
PA	Pipe Liner	–0.5–0.5	–0.5–0.2		
Acetal	Molded Parts	1	0		
HDPE	Flexible Pipe	10.7	10.9		
Fiberglass	Rigid Pipe	–0.43	–1.3–2.3		
Fiberglass	Tank	–0.02	–0.51		

^a ASTM Fuel C: 50 % iso-octane + 50 % toluene^b Swelling of the most common materials used in the class of polymers**Table K.5** Swelling of polymers in neat oxygenates [89]

Polymer	Application	Swelling, % vol.				
		MTBE	ETBE	TAME	CH ₃ OH	C ₂ H ₅ OH
NBR	Hose	36			14	11
FKM	Seal	59 – 180 ^a	3 – 10; 5 ^a	19 – 84; 70 ^a	16 – 135 ^a	2 ^a
FSI	Seal				5	6
CO, ECO					31	2
U	Seal		8		18	19
CSPE					1	1
CIIR					–4	
CPE					–2	
PS	Sealant				3	

^a Swelling of the most common materials used in the class of polymers

Table K.4 summarizes by class the swelling ranges of some polymers in model blends.

ASTM Fuel C (50 % iso-octane + 50 % toluene) with and without added oxygenates. Addition of 15 % vol. MTBE does not significantly change the performance of FKM (Viton) and NBR (Buna-N) elastomers commonly used for seals and hoses, respectively. That is, the swelling of FKM seals remains below 20 % vol. and the swelling of NBR-based hose materials may actually decrease somewhat. However, addition of 10–15 % vol. CH₃OH may compromise the integrity of some components by increased swelling of common polymers beyond acceptable limits set for certain seal and/or hose applications.

Table K.5 summarizes by class swelling data for some polymers exposed to neat oxygenates. Neat MTBE and neat CH₃OH are both aggressive swelling agents for FKM (Viton) whereas they are less aggressive toward NBR-based elastomers.

Table K.6 Swelling (% vol.) of some polymers and fiberglass in MTBE-ASTM Fuel C^a blends [89]

Polymer		Volume percent MTBE in ASTM Fuel C									
Name	Type	0	5	10	15	20	25	50	75	100	
Aflas-57 ^{b, c}	Elastomers	34	38	36	41	42				57	
NBR-34 ^c		37	37	38	38	38				36	
FSI ^d			22	23	24	26					
U ^e		27		19	24						
NBR		23		22	19						
FKM-66 ^c		15	17	15	18	20				180	
FKM-66 ^f		5					22	37	84	126	
FKM-65 ^f		8					26	43	105	153	
FKM-67 ^f		5					17	17	53	87	
FKM-68 ^f		4		6	7		16	29	65	88	
FKM-70 ^f		3					3	21	38	59	
FKM ^c		3	3	3	3	2				3	
ETP ^g										26	
HDPE	Thermoplas- tics	10.7			10.9						
PA-6,12		0.5			0.2						
PA-66		-0.5			-0.5						
Acetal		1			0						
Fiberglass pipe	Thermosets	-0.4			-1.3 to 2.2						
Fiberglass tank		-0.02			-0.51						

^a ASTM Fuel C: 50% iso-octane + 50% toluene^b Aflas-57—Fluoropolymer TFE-P dipolymer type^c Immersion for 140 days. FKM (Viton)—percent of fluorine^d 60°C^e U urethane^f Immersion for 7 days. FKM (Viton)—percent of fluorine^g ETP—Viton ETP (Extreme™)—67% fluorine**Table K.7** Swelling (Immersion for 140 days) (% vol.) of Fluoroelastomers FKM in ETBE-ASTM Fuel C (ASTM Fuel C: 50% iso-octane + 50% toluene) and TAME-ASTM Fuel C [89]

Elastomer ^a	Swelling (% vol.)						
	ETBE (% vol.)					TAME (% vol.)	
	in ASTM Fuel C						
	0	25	50	75	100	10	100
FKM-65	8	8	9	9	10	11	84
FKM-66	5	4	5	5	5	6	70
FKM-67	5	6	7	7	8	7	41
FKM-68	4	4	5	5	5	6	51
FKM-70	3	2	3	2	3	2	19

^a FKM (Viton)—percent of fluorine

Table K.8 Swelling (% vol.) of some polymers and fiberglass in Methanol-ASTM Fuel C (ASTM Fuel C: 50 % iso-octane + 50 % toluene) blends [89]

Polymer		Volume percent Methanol in ASTM Fuel C							
Name	Type	0	10	15	20	25	50	85	100
FSI ^a	Elastomers	16–25	22	25–30		26	25	9–15	5–9
PS		27	28						3
FKM-65		7		32			75	120	
FKM-66		1–5	21	30–46			57	85	100–135
FKM-67		14		14		24	16	13	16
FKM-68		5		15–30			20	22	20
FKM-70				7–19			8	4	
NBR-34		47–51	81	59	82		37	15	14
NBR-40		29	57	62	57				13
HNBR-36		23		60			38	14	
NBR-PVC		28			49				
NBR-BIIR		95			106				
NBR-CSM		56			82				
CO	Thermo-plastics	35		80			70	45	
ECO		33–40	77	95			75	50	31
Hypalon ^b		61	66						1
CIIR		96	81						–4
CPE		84	87						–2
U ^c		22	45–58						11–18
Fiberglass tank	Thermosets							10	

^a 60 °C^b Hypalon CSM (chlorosulphonated polyethylene)^cU - Polyester urethane**Table K.9** Swelling (% vol.) of some elastomers in Ethanol-ASTM Fuel C (50% iso-octane + 50% toluene) blends [89]

Elastomer	Volume percent Ethanol in ASTM Fuel C					
	0	10	15	20	25	100
FSI	16–18	19–22	20			6
FKM-65	7	23				
FKM-66	5	21	7			2
FKM-67	14	14				
FKM-68	5	17	24			
FKM-70	1	12	18			
NBR-34	51	68			99	11
NBR-36	23	58				
NBR-40	29	22				
HNBR-36	55	22				
NBR-PVC	28	34				
NBR-BIIR	95	70				
NBR-CSM	56	65				
CO	35	50				2
ECO	40	50				
Hypalon	61	81				1
U	21	51		56		19

Table K.10 Swelling (% vol.) of some elastomers in methanol, ethanol and MTBE blends with gasoline [92, 93]

Elastomer	Swelling ^a (% vol.)						
	Gasoline		Methanol	Ethanol	90% Gasoline + 10% of		
	Neat ^b	Spiked ^c to 50% aromatics			Methanol	Ethanol	MTBE
Fluorocarbon (FKM)	0	3	100	2	27	3	2
Polyester urethane (U)	11	23	18	19	42	37	13
Fluorosilicone (FMQ)	14	16	8	6	21	18	–
Butadiene acrylonitrile (NBR)	34	55	14	8	53	51	34
Polyacrylate (ACM)	44	120	94	101	112	136	–
Chlorosulphonated polyethylene (CSM)	49	74	1	1	41	56	48
Ethylene propylene diene terpolymer (EPDM)	137	143	0	13	109	124	139
Natural rubber (NR)	169	197	1	2	148	176	–

^a After 72 h immersion

Polymers are considered fuel resistant if the volume swell percent is less than about 30% [93]

^b Gasoline used was Indolene HO-III (model gasoline contained 30 % aromatics)^c Spiked with toluene

Materials are considered fuel resistant if the volume swell percent is less than 20–30 % (see Sect. 6). The swelling power of ethers are reduced as they are diluted into the nonpolar gasoline whereas the swelling power of alcohols are not reduced. The absorption characteristics of neat oxygenates are important indicators for the tendency of solvents to permeate polymer membranes. ETBE swells FKM (Viton) and urethane (U) elastomers far less than MTBE or even TAME. Since TAME is an isomer of ETBE, the stereochemistry of the oxygenates plays an important role in the swelling and permeation characteristic in FKM (Viton). Alcohols are more aggressive to polymers than ethers.

Appendix L: Coatings for Anticorrosion Protection of Tanks and Pipelines

Table L.1 Coating systems for anticorrosion protection of inner surfaces of tanks containing crude oil and fuels (Compatible also to gasoline containing oxygenates (MTBE to 15 % vol.) and aromatics (BTX to 35 % vol.)).

No.	Generic type ^a	Thickness, μm
1	Epoxies of various cross-linkers	200–1,500
2	Polyvinylchloride	200
3	Silicone-epoxy	250
4	Glass flake epoxy phenolic	250
5	Epoxy Solventless ^b	250–400
6	Epoxy phenolic	300–600
7	Epoxy novolac	200–400
8	Polysiloxane	300
9	Polyurethane	500
10	Epoxy reinforced with glass and mineral flakes	500
11	Glass filled epoxy with rust convertor, corrosion inhibitor and passivator	600
12	Vinyl ester with acrylic copolymer	1,250
13	Epoxy vinyl ester	1,500
	Vinyl ester	1,500

Surface preparation—Sa 2.5 [94]

^a Non-conductive coatings. Conductive and anti-static coatings are given in Table L.2

^b 100 % solids

Table L.2 Coating systems for anticorrosion protection of inner surfaces of tanks containing gasoline and naphtha

No.	Generic type	Thickness, μm	Antistatic properties
1	Solvent free amine cured epoxy (pigmented)	300–400	Electrically conductive
2	Epoxy with conductive powder and fillers	300–500	Anti-static ($10^5 \Omega$)
3	Inorganic zinc silicate	75–150	Anti-static

Surface preparation—Sa 2.5 [94]

Table L.3 Coating systems for anticorrosion protection of outer surfaces of tanks (roofs and shells) containing crude oil and fuels

No.	Generic type	Surface preparation	Thickness, μm	
			Each layer	Total
1	Surface Tolerant Epoxy Mastic (polyamide epoxy)	St2	125	300
	Surface Tolerant Epoxy Mastic (polyamide epoxy)		125	
	Polyurethane acrylic		50	
2	Surface Tolerant Epoxy Mastic (polyamide epoxy)	Sa 2.5	125	300
	Surface Tolerant Epoxy Mastic (polyamide epoxy)		125	
	Polyurethane acrylic		50	
3	Epoxy primer HB ^a	Sa 2.5	125	300
	Epoxy HB		125	
	Polyurethane		50	

Surface preparation [94]:

Sa 2.5—near-white metal blast cleaning

St2—mechanical cleaning; old paint and dense rust are remained on the surface

^a HB High-build epoxy

Table L.4 Protective coating systems for carbon steels under thermal insulation [95]

No.	Coating system	Thickness, μm		Surface		Temperature Range, $^{\circ}\text{C}$
		Each layer	Total	Preparation	Profile, μm	
1	High-build epoxy	130	260	NACE No. 2/ SSPC-SP10 ^a	50–75	–45 to 60
	Epoxy	130				
2	Fusion-bonded epoxy ^b	300	300		50–75	
3	Epoxy phenolic ^c	100–150	200–300	NACE No. 2/ SSPC-SP10 ^a	50–75	–45 to 150
	Epoxy phenolic ^d	100–150				
4	Epoxy novolac or silicone hybrid ^e	100–200	200–400	NACE No. 2/ SSPC-SP10 ^a	50–75	–45 to 205
	Epoxy novolac or silicone hybrid ^d	100–200				
5	Thermal-sprayed aluminum ^e	300–375	300–375	NACE No. 1/ SSPC-SP5 ^f	50–100	–45 to 595
6	Inorganic copolymer or coatings with an inert multipolymeric matrix ^c	100–150	200–300	NACE No. 2/ SSPC-SP10 ^a	40–65	–45 to 650
	Inorganic copolymer or coatings with an inert multipolymeric matrix ^d	100–150				
7	Thin film of petrolatum or petroleum wax primer Petrolatum or petroleum wax tape		1,000–2,000	SSPC-SP2 ^g or SSPC-SP3 ^h	–	60 (maximum)

^a Near-white metal blast cleaning (equivalent to Sa 2.5) [94]

^b Shop application only

^c First layer (prime coat)

^d Second layer (finish coat)

^e Minimum of 99% Al. Optional: sealer with either thinned epoxy or silicone coating depending on maximum service temperature (40 μm thickness)

^f White metal blast cleaning

^g Hand tool cleaning

^h Power tool cleaning

Table L.5 Protective coating systems for stainless steels^a under thermal insulation [95]

No.	Coating System	Thickness, μm		Surface Profile ^b , μm	Temperature Range, $^{\circ}\text{C}$
		Each layer	Total		
1	High-build epoxy	125–175	125–175	50–75	–45 to 60
2	Epoxy phenolic ^c	100–150	200–300	50–75	–45 to 150
	Epoxy phenolic ^d	100–150			
3	Epoxy novolac ^c	100–200	200–400	50–75	–45 to 205
	Epoxy novolac ^d	100–200			
4	Air-dried silicone or modified silicone ^c	37–50	74–100	15–25	–45 to 540
	Air-dried silicone or modified silicone ^d	37–50			
5	Inorganic copolymer or coatings with an inert multipolymeric matrix ^c	100–150	200–300	40–65	–45 to 650
	Inorganic copolymer or coatings with an inert multipolymeric matrix ^d	100–150			
6	Thermal-sprayed aluminum ^c	300–375	300–375	50–100	–45 to 595
7	Aluminum foil wrap	Min 64	Min 64	^e	–45 to 540

^a Austenitic and duplex stainless steels. The duplex stainless steels are not recommended for use above 300 $^{\circ}\text{C}$

^b Surface preparation must be done according to SSPC-SP 1 Solvent Cleaning and abrasive blast with nonmetallic grit such as silicone carbide, garnet, or virgin aluminum oxide. Solvent Cleaning is intended for removal of all visible oil, grease, soil, drawing and cutting compounds, and other soluble contaminants from steel surfaces with solvent, vapor, cleaning compound, alkali, emulsifying agent, or steam [96]

^c First layer (prime coat)

^d Second layer (finish coat)

^e Surface preparation must be done according to SSPC-SP 1 Solvent Cleaning. Minimum of 99% aluminum. Optional: sealer with either thinned epoxy or silicone coating depending on service temperature (40 μm thickness)

Table L.6 Coatings for anticorrosion protection of outer surfaces of underground pipelines and tanks

No.	Coating System	Thickness, μm		Surface preparation
		Each layer	Total	
1 ^a	Fusion Bonded Epoxy	450	2,150–	Sa 2.5 ^c
	Stabilized Adhesive Polypropylene	200	3,150 ^b	
	Copolymer Stabilized	1,500–2,500 ^b		
	Polypropylene or Polyethylene			
2	Epoxy Solventless ^d	750	750	Sa 2.5 ^c
3	Polyurethane ^d	550	550	Sa 2.5 ^c
4	Surface tolerant aluminum mastic epoxy	80	1,580	Sa 2.5 ^c
	Polyurea	1,500		
5 ^e	Epoxy polyamine primer	50	800	Sa 2.5 ^c
	Urethane modified highly flexible epoxy	250		
	Urethane modified highly flexible epoxy	250		
	Urethane modified highly flexible epoxy	250		
6 ^f	Epoxy polyamide universal primer	50	550	Light sand blasting (15 μm surface profile)
	Urethane modified highly flexible epoxy	250		
	Urethane modified highly flexible epoxy	250		

Systems 2–5 may be used to 120 $^{\circ}\text{C}$

All coating systems are compatible with cathodic protection

^a Shop application only

^b Depends on the diameter of pipe

^c Near-white metal blast cleaning [94]

^d 100% solids

^e Only for repair

^f For galvanized steel

Postscript...Insight into the Future ...

"How pleasant to know, that you learned something new!"

Jean-Baptiste Poquelin Moliere (1622–1673), a French play writer and actor

We have made a long way in learning the properties of crude oil, petroleum products, fuels, fuel additives, biofuels, and their influence on metals and polymers which are used in systems for their transportation and storage. In order to prevent catastrophes related to corrosion of metallic structures and equipment, destruction of polymeric materials, deterioration of fuels and environment we should know the behavior of all these materials in contact with fuels and other environments such as atmosphere, soil, and water, including microorganisms.

We live in the world of paradoxes and myths. It is not simple to set a myth apart from reality.

An example of this is the opinion of many chemists that crude oils and fuels are not corrosive. However, in practice we encounter the real opposite situation. I hope that after reading this book it became clearer in what cases corrosion in contact with fuels could occur, how it could be prevented and controlled.

People name each era according to main material they use: the Stone Age, the Bronze Age, the Iron Age ... or according to main source of energy and fuel: the Coal Age, the Petroleum Age. It is possible to call our era the Metal-Polymer-Petroleum Age. We are eyewitnesses that the Age of Biofuels and Natural Gas is coming. In spite of this, crude oil will remain the main source of liquid fuels in the nearest future. Certainly biofuels will be increased in use. Therefore tanks, pipelines and other systems made from different metals, polymeric and composite materials will be used in contact with crude oil, fuels and new biofuels. It is unlikely that we will be able to eliminate all the causes of corrosion. It would be naive to think that we can win corrosion. It is unnatural, since it is contrary to the Second law of thermodynamics that governs all processes in the universe. The problem of corrosion is eternal. We will live with it forever until metals and environment exist. But we will penetrate deeper and deeper into understanding of corrosion, and hence new ways of prediction and control will be found in many cases.

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Glossary

Aboveground storage tank (AST) a stationary container, of greater than 60 m³ capacity usually cylindrical in shape, consisting of a metallic roof, shell, bottom, and support structure where more than 90% of the tank volume is above surface grade.

Additives (to fuels; Fuel additives) chemical compounds added in small amounts to finished fuel products to improve their certain properties.

Alcohol an organic compound in which the hydroxyl functional group (–OH) is bound to a carbon atom. The general formula: C_nH_{2n+1}OH, e.g., ethanol C₂H₅OH.

Aldehyde an organic compound containing a functional group CHO with the general formula R–CHO.

Alkanes (paraffins, saturated hydrocarbons) chemical compounds consisting only of carbon and hydrogen atoms and are bonded exclusively by single bonds. The general formula: C_nH_{2n+2}.

Alkenes (olefins, unsaturated hydrocarbons) chemical compounds consisting only of carbon and hydrogen atoms and containing one or more pairs of carbon atoms linked by a double bond. The general formula: C_nH_{2n}.

Alkoxylated polyglycols alkoxylated alcohol (organic compounds); can be used as non-ionic surfactant (detergent, cleaning), lubricant, drilling fuel additive in oil and gas applications.

Alkyl a functional group R- (radical—C_nH_{2n+1}), e.g., CH₃–, C₂H₅–.

Alkylphenols organic compounds; derivatives of phenol having one or more alkyl groups attached to the carbon ring.

Amides organic compounds with the functional group RY(O)_xNR' where R and R' refer to H or radical; Y=carbon or sulphur or phosphorous atoms.

Amines organic compounds; derivatives of ammonia, where in one or more hydrogen atoms have been replaced by an alkyl or aryl (C₆H₅–) group.

Amine carboxylates carboxylate salts of amines (amine salts of carboxylic acids).

Amphoteric metals metals that corrode in acidic and alkali aqueous solutions.

Anthraquinone an aromatic organic compound.

Antiknocks an antiknock agent is a gasoline additive used to reduce engine knocking and increase the fuel's octane rating by raising the temperature and pressure at which ignition occurs.

Antioxidants substances that inhibit oxidation of hydrocarbon components of fuels.

Aromatic diamines organic compounds with two amino groups.

Aromatic ring the configuration of six carbon atoms in aromatic compounds; is known as a benzene ring.

Aromatic solvents (aromatics) aromatic compounds based on benzene ring.

Aryl sulphonates salts or esters of sulphonic acids (surfactants).

Asphalt (bitumen) a sticky, black and highly viscous liquid or semi-solid material (mixture of high molecular weight hydrocarbons).

Asphaltenes heterocyclic aromatic compounds containing N, S and O atoms.

Auto-ignition temperature the lowest temperature at which a compound will spontaneously ignite in a normal atmosphere without an external source of ignition.

Aviation fuels (avfuels) a type of fuel used to power aircraft; it may be of two types: avgas (gasoline, *aviation spirit* in the UK, used to power piston-engine aircraft) and turbine jet fuel (kerosene).

Azo compounds compounds $R-N=N-R'$ (the $N=N$ group is called an azo group) in which R and R' can be either aryl or alkyl.

Bacteria (microorganisms) large domain of microorganisms; a few microns in length, bacteria have a wide range of shapes, ranging from spheres to rods and spirals.

Benzene an aromatic hydrocarbon with the molecular formula C_6H_6 ; a natural constituent of crude oils.

Biodegradation capability of being broken down by the action of microorganisms.

Bioalcohol organic compound (alcohols) obtained from biological materials and/or biological processes. There is no difference in chemical structure between biologically and chemically produced alcohols.

Biocide a substance for killing microorganisms.

Biodegradation destruction of materials by microorganisms.

Biodiesel a fuel suitable for use in compression ignition (diesel) engines that is made of fatty acid monoalkyl esters (FAME or FAEE).

Bioethanol ethanol obtained from biological materials or fermentation.

Biofouling (slime, sludge) biological fouling, the accumulation of microorganisms, plants, algae or animals on wetted surfaces.

Biofuels fuels derived from biomass conversion.

Biomass biological material from living, or recently living organisms, most often referring to plants or plant-derived materials.

Bitumen a sticky, black and highly viscous liquid or semi-solid material (mixture of high molecular weight hydrocarbons).

Bituminous coal (black coal) a relatively soft coal containing bitumen.

Boiling range the range of temperature over which a fuel, or other liquid mixture of compounds, distills.

Brass an alloy consisting of copper and zinc (15–50 wt% Zn).

Bronze an alloy consisting primarily of copper and tin (~10 wt% Sn) as the main additive.

Carbon steel an alloy containing iron (Fe) and carbon (C) at concentrations from 0.008 to 2 wt%, and small amounts of other elements.

Carboxylic acids organic acids containing at least one carboxyl group -COOH .

Carcinogenic producing or tending to produce cancer.

Cathodic protection a technique used to control the corrosion of a metal surface by making it the cathode (which does not corrode) of an electrochemical cell.

Cetane number a measure of the ignition quality of diesel fuel based on ignition delay in an engine.

Chelating compound a fuel additive that deactivates the catalytic oxidizing action of dissolved metals (mainly copper) on fuels during storage.

Chlorophyll a green pigment found in cyanobacteria and the chloroplasts of algae and plants. Its name is derived from the Greek words *chloros* (green) and *phyllon* (leaf).

Coal tar a mixture about 200 substances (phenols, polycyclic aromatic hydrocarbons, and heterocyclic compounds); a brown or black liquid of extremely high viscosity.

Cloud point the temperature at which a sample of a fuel just shows a cloud or haze of wax (or in the case of biodiesel, methyl ester) crystals when it is cooled under standard test conditions, as defined in ASTM D2500.

Coalescence a process of uniting small droplets of one liquid preparatory to its being separated from another liquid (separation of emulsion).

Coalescer a device performing coalescence.

Coating disbondment the destruction of adhesion between a coating and the surface coated.

Colloid a substance microscopically dispersed evenly throughout another substance.

Composite materials (composites) materials made from two or more components with significantly different physical and chemical properties, that when combined, produce a material with characteristics different from the individual components.

Conductivity Unit (CU) unit of electrical conductivity of fuels. $1 \text{ CU} = 1 \text{ pico Siemens/meter} (1 \text{ pS/m}) = 1 \cdot 10^{-12} \text{ Ohm}^{-1} \cdot \text{m}^{-1}$.

Corrosion inhibitors chemicals that, when present in low concentrations (1–15,000 ppm) in a corrosive environment, retard the corrosion of metals.

Crude oil a liquid mixture of different hydrocarbons that exist in the Earth's crust.

Cyclic amines organic compounds with N atoms inside the cycle.

Cycloalkanes (cycloparaffins, naphthenes) types of saturated hydrocarbons that have one or more rings of carbon atoms in the chemical structure.

Cycloparaffins types of saturated hydrocarbons that have one or more rings of carbon atoms in the chemical structure.

Demulsifiers (detergents, surfactants, emulsifiers, emulgents, wetting agents) substances (polar compounds) that cause a marked reduction in the interfacial tension of liquids.

Dew point the temperature, at which the moisture content in the air will saturate the air.

Diens chemical compounds consisting only of carbon and hydrogen atoms and containing two pairs of carbon atoms linked by a double bond.

Diesel fuel (diesel oil, gas oil, heating oil, or petrodiesel) a liquid mixture of hydrocarbons C_{12} to C_{24} distilled in the range 180–370 °C.

Dispersant a surfactant additive designed to hold particulate matter dispersed in a liquid.

Distillation (rectification) a process of separating a liquid homogeneous mixture into fractions based on differences in boiling points of its components.

Elastomer synthetic rubber-type polymer material.

Electrolytes are the substances whose water solutions or molten states conduct electric current on account of free ions.

Emulsion a two-phase system of a mixture of two or more immiscible liquids.

Ester organic compound containing the group COO combining with two radicals.

Ethanol C_2H_5OH (alcohol).

Ether organic compound where two radicals are bonded through oxygen atom.

Ethyl mercaptan an organic compound C_2H_5SH (ethanthiol) added to the propane—butane gas in order to detect the leakage of the latter according to its specific unpleasant odour.

Eutectic a mixture of chemical compounds or elements that have a single chemical composition that solidifies at a lower temperature than any other composition made up of the same ingredients.

Fatty acids saturated monocarboxylic acids.

Fatty acid methyl ester (FAME) mono alkyl ester of long-chain fatty acid.

Fiberglass a composite material, a glass reinforced plastic.

Flash point the lowest temperature at which the vapors above a flammable liquid will ignite on the application of an ignition source; the temperature at which liquid fuel will generate a flammable vapor near its surface.

Fuel oil a liquid mixture of hydrocarbons ($>C_{20}$) with boiling point $>340^\circ C$.

Fungi microorganisms including yeasts and molds (more familiar as mushrooms).

Gas oil a liquid mixture of hydrocarbons C_{12} to C_{24} distilled in the range $180\text{--}370^\circ C$.

Gasoline (Gas, Petrol) a liquid mixture of hydrocarbons (C_4 to C_{12} , with the most prevalent C_8) boiling between 20 and $210^\circ C$.

Grease a semisolid lubricant.

Gum polymerized organic materials of high viscosity formed during fuel storage.

Gunitite the concrete that is blasted by pneumatic pressure from a gun.

Hindered phenols phenols containing side branched alkyls.

Hydrocarbons compounds composed only of hydrogen (H) and carbon (C) atoms.

Hydrosulfurization the process of removing hydrogen sulphide (H_2S) and other sulphur- organic compounds from petroleum products at the oil refineries.

Hydroperoxides organic compounds $R-O-O-H$.

Hydrophilic water accepting. *Hydros* (from the Greek) means *water*; *philia* means *love*.

Hydrophobic water repelling. *Hydros* (from the Greek) means *water*; *phobos* means *fear*.

Hydrotreating treatment with hydrogen.

Immiscible liquids which are mutually insoluble.

Ketones organic compounds where two radicals are bonded with the group $C=O$.

Kerosene (jet fuel, aviation kerosene, aviation fuel) a liquid mixture of hydrocarbons C_9 to C_{16} boiling at 150–290 °C.

Liner a system or device, such as a membrane, installed beneath a storage tank, in or on the tank dike, to contain any accidentally escaped product.

Litharge one of the natural mineral forms of lead (II) oxide PbO ; it forms as red coating.

Lubricant a substance introduced to reduce friction between moving surfaces.

Lubricity an ability to reduce friction between solid surfaces in relative motion.

Membrane a thin, continuous sheet of nonconductive synthetic material used to contain and/or separate two different environments.

Mercaptans a sulphur-containing organic compound where radical is combined with the group $-SH$.

Methyl tertiary-butyl ether (MTBE) oxygenate.

Microbial metabolism the set of life-sustaining chemical transformations within the cells of living organisms.

Minium (red lead, lead (II, IV) oxide Pb_3O_4) mineral, natural pigment used in rust-proof primer paint for iron objects.

Miscible liquids which are mutually soluble.

Mold (mould) a fungus that grows in the form of multicellular filaments.

Monoaromatics hydrocarbons having a single aromatic ring.

Naphthenates salts of naphthenic acids.

Naphthenes types of saturated hydrocarbons that have one or more rings of carbon atoms in the chemical structure.

Naphtha the lightest and most volatile distillate fraction of the liquid hydrocarbons in crude oil.

Neutralization Number a measure of the numbers of milligrams of potassium hydroxide (KOH) needed to neutralize 1 g of crude oil or its distillate fraction.

Nitrile butadiene rubber (NBR, Buna-N) elastomer.

Non-polar hydrocarbons molecules which have symmetry.

Nutrients chemical substances that organisms need to live and grow.

Octane number (rating) the percentage (by volume) of iso-octane in a combustible mixture.

Oil shale (kerogen shale) an organic-rich fine-grained sedimentary rock containing kerogene from which liquid hydrocarbons can be produced.

Olefins chemical compounds consisting only of carbon and hydrogen atoms and containing one or more pairs of carbon atoms linked by a double bond. The general formula: C_nH_{2n} .

Oxidative stability the ability of a fuel to resist oxidation during its storage.

Oxygenated fuels fuels containing oxygenates (*ethers* and *alcohols*) for increase their octane number, better burning, and reducing vehicle emissions.

Oxygenates organic compounds containing oxygen and are added to gasoline to boost its octane number, promote cleaner fuel combustion, and reduce vehicle emissions.

Paraffins chemical compounds consisting only of carbon and hydrogen atoms and are bonded exclusively by single bonds. The general formula: C_nH_{2n+2} .

Peroxides organic compound where two radicals are bonded through the peroxide functional group—O—O—.

Petrodiesel a liquid mixture of hydrocarbons C_{12} to C_{24} distilled in the range 180—370 °C.

Petrol a liquid mixture of hydrocarbons (C_4 to C_{12} , with the most prevalent C_8) boiling between 20 and 210 °C.

Phenols organic compounds containing aryl combining with one or more group OH.

Photosynthesis a process used by plants and other organisms to convert the light energy captured from the sun into chemical energy.

Pig a device that moves through the inside of a pipeline for the purpose of cleaning, dimensioning, or inspecting.

Pigging the process of forcing a solid object (pig) through a pipeline.

Plankton microscopic organisms that float in liquids.

Polar hydrocarbons molecules which have no symmetry and contain in addition to hydrogen and carbon, hetero atoms.

Polymer a material consisting of repeating units (group of atoms).

Pontoon an air-filled metal (carbon steel or aluminum alloy) structure providing buoyancy (floating roof is installed on pontoon in AST).

ppm parts per million (weight concentration); 1 mg of substance in 1,000,000 mg = 1,000 g = 1 kg of liquid solution.

ppb parts per billion (weight concentration); 1 mg of substance in 1,000,000,000 mg = 1,000,000 g = 1,000 kg of liquid solution.

Porphyrins nitrogen containing compounds derived from chlorophyll and occur as organometallic complexes of vanadium and nickel in crude oils.

Rectification a process of separating a liquid homogeneous mixture into fractions based on differences in boiling points of its components.

Relative humidity the percentage of water vapor present in air, relative to the maximum amount of water that the air (saturated by water) can hold at the same temperature.

Shellac is a natural polymer.

Secondary containment a device or system used to control the accidental escape of a stored product so it may be properly recovered or removed from the environment.

Slime biological fouling, the accumulation of microorganisms, plants, algae or animals on wetted surfaces.

Slops liquid wastes (emulsion) containing mixtures of various fuels and water.

Soda ash (washing soda, sodium carbonate) Na_2CO_3 .

Sodium naphthenate surfactant.

Stainless steel an alloy of iron with chromium content above 12 wt%.

Succinimide a cyclic imide (organic compound).

Sulfonate a salt or ester of sulfonic acid (surfactant).

Surfactants (surface active agents) substances (polar compounds) that cause a marked reduction in the interfacial tension of liquids.

Suspension a heterogeneous mixture containing solid particles (usually larger than 1 mm) in liquid.

Tank cushion (tank pad) the material immediately adjacent to the exterior steel bottom of an aboveground storage tank.

Teflon brand name of polytetrafluoroethylene (PTFE).

Terne an alloy coating that was historically made of lead (80 wt%) and tin (20 wt%) used to cover steel. Nowadays lead is replaced with zinc (50 wt%).

Tetra-ethyl lead (TEL) the first anti-knock additive to gasoline.

Toluene organic aromatic solvent.

Total Acid Number (TAN; Neutralization Number) a measure of the numbers of milligrams of potassium hydroxide (KOH) needed to neutralize 1 g of crude oil or its distillate fraction.

Viton a brand of synthetic rubber and fluoroelastomer. The fluorine content varies between 66 and 70%.

Waxes chemical compounds that are plastic (malleable) at ambient temperatures.

White spirit high boiling fraction of gasoline (130–200 °C).

Wide-cut jet fuel (avtur) kerosene-naphtha or kerosene-gasoline blends.

Yeasts microorganisms in the kingdom Fungi.

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